Potential and problems related to reuse of water in households

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PREFACE

This Ph.D. thesis is the result of three years' work at Environment & Resources DTU, the Technical University of Denmark, as a part of the completion of the Ph.D. degree. The work was carried out in the period from August 1999 to October 2002. Associate Professor Dr. Anna Ledin, and Professor Mogens Henze acted as supervisors. The thesis consists of a summary focussed on developing a methodology for identifying hazards and problems related to the reuse of non-potable water within households, with the emphasis on xenobiotic organic compounds. It is based on the following 7 papers. Four of these have been submitted to international peer-reviewed journals and the rest are draft manuscripts intended for publication. However, the listed papers are not included in the www-version but can be obtained from the library at Environment & Resources DTU, Bygningstorvet, Building 115, Technical University of Denmark, DK-2800 Lyngby (e-mail library@er.dtu.dk).

I. Eriksson, E. Auffarth, K.P, Henze, M. and Ledin, A. (2002) Characteristics of grey wastewater. *Urban Water* 4 (1): 85-104.

II. Eriksson, E., Albrechtsen, H. -J., Auffarth, K., Baun, A., Boe-Hansen, R., Mikkelsen, P.S., and Ledin, A. Heavy metals and xenobiotic organic compounds in stormwater run-off, draft manuscript intended for publication

III. Eriksson, E., Auffarth, K., Eilersen, A. -M., Henze, M. and Ledin, A**.** (2003) Household chemicals and personal care products as sources of xenobiotic organic compounds in grey wastewater. *Water SA* 29 (2): (in press).

IV. Eriksson, E., and Ledin, A. Analysis of long-chain fatty acids in grey wastewater with in-vial-derivatisation. Submitted to *Water Research*

V. Eriksson, E., Baun, A., Henze, M. and Ledin, A. Environmental risk assessment of xenobiotic organic compounds in grey wastewater (Denmark), manuscript intended for publication

VI. Eriksson, E., Baun, A., Mikkelsen, P. S., and Ledin, A. Environmental and health hazard identification of chemical substances in rainwater collected for non-potable use in households, manuscript intended for publication.

VII. Eriksson, E., Baun, A., Henze, M. and Ledin, A. Phytotoxicity tests of grey wastewater to green algae and willow trees. Submitted to *Ecological Engineering*

All references to these papers are highlighted by bold italic roman numerals (***I-VII***)

This study was funded by a Ph.D. grant from the Technical University of Denmark.

Kgs. Lyngby October 31, 2002.

Eva Eriksson

SUMMARY

There is a growing demand in society for the introduction of decentralised sanitary reuse systems and the main reason for this is that centralised urban sanitation systems are expensive and resource-intensive. A second is water shortage and one way to reduce the need for freshwater is to reuse wastewater on-site. One possibility for recycling is to use grey wastewater or rainwater for non-potable purposes. Very little is currently known of the presence of xenobiotic organic compounds (XOCs) in these water fractions. Knowledge of the type of constituents present, concentration ranges and of any potential risk they may pose are all-important issues when discussing local handling e.g. on-site reuse as well as discharge into receiving water.

We are exposed to thousands of compounds in our daily life as over one hundred thousand compounds are on the market in the European Union, with 30,000 being used in volumes of over 1 ton per annum. Pharmaceuticals, household chemicals, personal care products, clothing, foodstuffs, additives, building materials, cars, industry, combustion and incineration are a few examples of the sources of chemical compounds in our environment.

The objective of the study is to develop a methodology for identifying compounds that might pose a threat in connection with the use of non-potable water in households or with discharges into the environment, with the focus on XOCs; and in addition to test the method in two different cases. The methodology used was to apply a number of different methods: research of literature, empirical studies incl. chemical analyses; specifically developed analysis methods; toxicity measurements, hazard and problem identification, and risk assessments. The battery of methods was applied to two selected cases, namely grey wastewater and collected rainwater.

It can be concluded that previous knowledge about the characteristics of grey wastewater (physical, chemical and biological constituents) is limited. The focus has been on the content of oxygen-consuming compounds, nutrients and micro-organisms, while information about the presence and levels of specific XOCs is very limited. It was also found that grey wastewater from different sources has different characteristics, which illustrates the need for different types of treatment before any recycling of the water.

XOCs that potentially are present in grey wastewater were listed based on information available on chemical products, consumption statistics and chemical databases as well as information on XOCs in wastewater. The list reached 900 different compounds and compounds groups.

201 different XOCs were identified in grey wastewater from bathrooms (showers and handbasins) by chemical analyses. Several fragrances such as citronellol, coumarin and hexyl cinnamic aldehyde were identified as well as some preservatives e.g. parabens and triclosan. The measurements also showed that bioactive chemicals (pharmaceuticals) were present, as well as unexpected compounds not directly derived from household chemicals e.g. flame retardants and drugs. The presence among others of detergents, softeners and preservatives was confirmed.

In an investigation of consumption of household chemicals in multi-family accommodation, 92 different household chemicals and personal care products were recorded. The inhabitants' average weekly consumption of chemicals was about 40 g per person. The inventory of household chemicals and personal care products listed registered a total of 290 chemical constituents. It was shown that it is possible to track the potentially toxic compounds used in households and which may present a problem, e.g. in relation to infiltration of grey wastewater. However, the observations made in this study illustrate that an inventory of the

use of household chemicals, although detailed and carefully carried out, cannot represent a full characterisation of the compounds actually present in grey wastewater.

In toxicity testing some types of grey wastewater (kitchen and laundry effluents) were found to be toxic to willow trees and freshwater green algae. The toxicity of the laundry effluent may be related to the toxicity of the detergents used.

A total of 39 compounds out of the 201 found to be present in the grey wastewater from bathrooms were listed as potentially problematic pollutants in environmental hazard identification, based on the inherent properties; persistence, bioaccumulation and toxicity. A large number of the compounds were also found to be health hazardous. An environmental risk assessment of the 201 compounds revealed that five compounds constitute a risk if discharged into surface water or into a soil bed.

For collected rainwater a large number of organic, inorganic, and microbiological constituents were found to be present. The data showed that there was significant variation between different sites due to different climate, urban environment, and land use. It was established that the majority of the studies focus on run-off from roads and roofs, as well as on unspecific stormwater. The number of constituents that were identified and quantified in collected rainwater is, however, probably only a fraction of those constituents that could be present, as a limited search of potential sources and their contribution resulted in a list of several hundreds of individual compounds.

Hazard identification based on environmental and health hazards revealed that the number of pollutants, which constitute a potential hazard with respect to the use of collected rainwater, is high. However, there was no evidence of any adverse effects on willows caused by three samples of collected rainwater.

Both health and environmental hazard identification were hampered by the lack of data on the identified compounds. However, the methodology used was found to be able to identify constituents that may constitute a problem both from constituents found to be observed or potentially present in the water fraction or from constituents detected in chemical analyses. The methodology can be refined and applied to other scenarios and could be extended to provide a realistic risk management tool.

RESUME

Efterspørgslen på decentraliserede sanitetssystemer med genanvendelse af spildevand er stadigt stigende. Hovedårsagen er, at byernes centraliserede systemer er dyre og ressource forbrugende både i anlæg og drift. En anden årsag er vandmangel, hvor genanvendelse af spildevand kan mindske indvindingen af ferskvand. Genanvendelse af gråt spildevand eller opsamlet regnvand er en mulighed. Meget lidt kendes til indholdet af xenobiotiske organiske stoffer (XOS) i gråt spildevand og afstrømmet regnvand, og der mangler generelt viden vedrørende forekomsten af denne type af forurening, koncentrationsniveauer samt hvorvidt disse stoffer udgør en potentiel risiko, når man diskuterer lokal håndtering, genanvendelse, og udledning til vandmiljøet.

Vi udsættes i vort daglige liv for tusindvis af kemikalier. Over hundredetusinde stoffer er markedsført inden for EU og ca. tredivetusinde af dem er såkaldte hverdagskemikalier. Forbruget af disse udgør alene mere end 1 ton årligt. Farmaceutiske præparater, husholdningskemikalier, produkter til personlig pleje, tøj, mad og additiver såvel som bygningsmaterialer, fx blødgørere og maling, biler, industri, motor forbrænding, og forbrændingsanlæg er nogle få eksempler på kilder til kemikalier i vores miljø.

Formålet med dette Ph.d. studie har været at udvikle en metode til at identificere stoffer som kan udgøre en trussel eller et problem ved genanvendelse af vand i husholdninger eller ved udledning til miljøet, og desuden at teste metoden på to forskellige cases, gråt spildevand og opsamlet regnvand. Fremgangsmåden har været at benytte flere forskellige metoder, herunder litteraturstudier, empiriske studier, kemiske analyser inkl. udvikling af analysemetoder, farligheds- og problem identificering, risikovurdering og toksicitetsmålinger. Fokus har været på de xenobiotiske organiske stoffer.

Det kan konkluderes, at den nuværende viden om den fysiske, kemiske og biologiske sammensætning af gråt spildvand er begrænset. Fokus har hidtil været på indholdet af iltforbrugende stoffer samt mikroorganismer, mens information vedrørende tilstedeværelse og koncentration af specifikke XOS er meget begrænset. Endvidere blev der fundet, at gråt spildevand har forskellig sammensætning afhængigt af kilderne, hvilket illustrerer behovet for forskellige typer af behandling inden genbrug.

En sammenstilling over XOS der potentielt kan forekomme i gråt spildevand resulterede i en liste med mere end 900 forskellige stoffer.

201 forskellige XOS blev identificeret i gråt spildevand fra badeværelse (brusebad og håndvask) med kvantitative og kvalitative analyser. Flere duftstoffer som citronellol, coumarin og hexyl cinnamic aldehyde, og konserveringsstoffer som fx parabener og triclosan blev identificeret. Målingerne viste også, at bioaktive stoffer (farmaceutiske stoffer) og stoffer, som ikke direkte kommer fra husholdningskemikalier, fx flammehæmmere, var til stede. Forekomsten af blandt andet detergenter, blødgørere, og konserveringsstoffer blev bekræftet af kvantitative analyser.

I en undersøgelse af forbruget af husholdningskemikalier i en beboelsesejendom blev 92 forskellige husholdningskemikalier og personplejeprodukter registreret. I gennemsnit blev der forbrugt ca. 40 g per person per dag. Ved aflæsning af indholdsfortegnelserne på produkterne blev i alt 290 kemiske parametre registreret. Det viste sig at være muligt at spore de potentielle toksiske stoffer brugt i husholdninger samt at identificere hvilke stoffer, der kan forårsage problemer ved fx nedsivning af gråt spildvand. Dette studie illustrerer dog, at selv en grundig og omhyggelig inventering af forbruget af husholdningskemikalier ikke kan kompensere for en fuld karakterisering af de stoffer, der faktisk forekommer i det grå spildevand.

I alt 39 af de 201 stoffer, der blev fundet i gråt spildvand fra badeværelser, blev registreret som potentielt problematisk forurenende stoffer i en miljøfarlighedsvurdering baseret på stoffernes iboende egenskaber; persistens, bioakkumulation og toksicitet. Et stort antal af stofferne blev yderligere klassificeret som sundhedsskadelige. En miljørisikovurdering af de 201 stoffer afslørede, at fem af stofferne udgør en risiko ved udløb til overfladevand eller nedsivning i jord. Ved toksicitetstest blev det påvist, at nogle typer af gråt spildvand (køkken- og vaskemaskineudløb) er toksisk for piletræ og ferskvandsalger. Toksiciteten af prøven fra vaskemaskiner kan måske være forbundet med toksiciteten af de detergenter, der blev brugt.

For opsamlet regnvand blev det konstateret, at et utal af organiske, uorganiske, og mikrobiologiske forureningsparametre var tilstede, i alt er det fundet ca. 600 parametre litteraturen. Forskelle i beliggenhed, klima, bymæssige næromgivelser, og overfladeanvendelse afspejles generelt i store variationer i data. Det blev fastslået at et flertal af undersøgelserne har fokuseret på afstrømning af regnvand fra veje og tage samt uspecificeret regnafstrømning. Antallet af forurenende stoffer, som er blevet identificeret og kvantificeret i opsamlet regnvand, er sandsynligvis kun en lille del af de stoffer, der faktisk kan være tilstede, da en begrænset undersøgelse af potentielle kilder og deres bidrag resulterede i en liste med flere hundrede forurenende stoffer. En farlighedsidentificering på basis af potentiel miljø- og sundhedspåvirkning afslørede, at antallet af forurenede stoffer, som muligvis kan udgøre en fare med hensyn til genanvendelse af opsamlet regnvand, er stort. Dog kunne der ikke konstateres nogen negativ effekt på pil ved vækstforsøg med tre forskellige prøver af opsamlet regnvand.

Både sundheds- og miljøfarlighedsvurderingen blev hæmmet af manglen på data for de identificerede stoffer. Den anvendte metode kunne dog identificere forbindelser, som potentielt kan udgøre problemer. Metoden til farlighedsidentificering kan videreudvikles og anvendes til andre scenarier end genanvendelse af gråt spildevand og opsamlet regnvand, og den kan endvidere udvides til en realistisk risikovurdering.

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1. INTRODUCTION

Mismanagement and contamination of the aquatic environment have been debated for about 40 years, since it became clear that the basic principle for urban water use, "to consume and contaminate", caused serious damage to receiving waters. Eutrophication in receiving waters, microbiological contamination, odour, death of aquatic organisms and foaming due to a surplus of detergents are a few of the effects that led to the development of wastewater treatment plants. These centralised urban sanitation systems that often receive both household and industrial wastewater along with rainwater may be very effective, but can also be expensive and resource-intensive. This is one example that can be used to illustrate why the discussion on building a more "sustainable" or "ecological" society was initiated. Another reason to look for alternative handling of wastewater is the water shortage, which is a problem in large parts of the world.

Reuse of wastewater can be seen as a water resource for non-potable purposes. In addition, separation of different water fractions e.g. surface run-off from the wastewater system can reduce the peak flow during a rain event and thereby reduce the risk to combined sewer overflows, as well as making it possible to collect and utilise the rainwater for non-potable purposes.

Very little is known about the presence of xenobiotic organic compounds (XOCs) in different wastewater and rainwater fractions. Knowledge of the type of constituents present and at what concentration levels, as well as whether they represent a potential risk are important issues when discussing local handling, e.g. on-site reuse as well as discharge into receiving water, as they might pose a threat to the inhabitants utilising the non-potable water or to the organisms within the recipient. The number of published studies focusing on different methods for reuse of grey wastewater, e.g. irrigation or indirect reuse by infiltration, is limited. The health aspects and economics of this type of alternative wastewater handling have been examined but no environmental hazard identification in respect of infiltration has been located.

1.1. RECLAMATION OF WATER

Water of drinking quality is not an endless resource and it is unevenly distributed throughout the world. Some areas are arid and water resources limited, and in other areas the water resources are insufficient for sustaining the growing population size. In addition, drinking water resources are abandoned of necessity as they have become polluted e.g. by nutrients and pesticides. Against this background, demand for saving water has risen, e.g. by using low-flushing toilets and using water of lower quality. In the industrialised world today we are mainly using water of drinking-water quality for toilet flushing and laundry where water of lower quality, e.g. grey wastewater or collected rainwater, is adequate for both these functions. Suggested non-potable reuse possibilities in households are urinal and toilet flushing, laundry and vehicle and window washing (Asano *et al*., 1996; Law, 1996). Fire protection and concrete production are examples of other suggested applications on a larger scale. Use of rain and wastewater for irrigation and infiltration into soil as well as to preserve and develop wetlands are obvious alternatives to discharge into receiving waters. (Gerba *et al*., 1995; Neal *et al*., 1995; Otterpohl *et al*., 1999) (See Figure 1a and b). There are, however, many questions concerning health risks, risk of environmental pollution, technical problems, financial profits, social acceptability etc.

1.1.1. Grey wastewater

The terms 'diluted', 'light' or 'grey' wastewater refer to wastewater produced in households, office buildings and schools as well as some types of industries, where there is no contribution from toilets or heavily polluted process water. Grey wastewater in households is

wastewater from baths, showers, handbasins, washing machines and dishwashers, laundries and kitchen sinks. This type of wastewater has been estimated to account for about 74% of the volume of residential sewage (Hansen and Kjellerup 1994).

1.1.2. Collected rainwater

Collected rainwater refers to run-off water collected from roofs, roads, parking lots, impervious urban areas, green or recreational areas and specific local sites e.g. airports: water which can be collected and stored for further use.

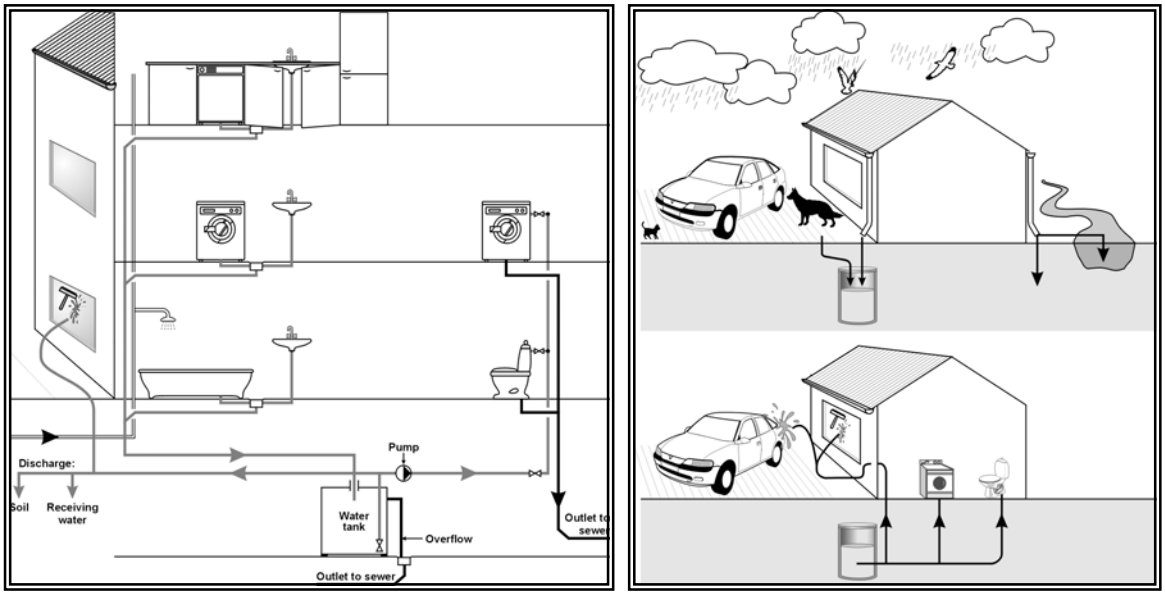

Figure 1a and 1b Alternative uses of a/ grey wastewater and b/ collected rainwater reclamation and utilisation in households (Toilet flushing, laundry, car, and window wash as well as discharge into the environment)

In Denmark, the use of rainwater for toilet flushing and washing of clothes is already legal for private residences and technical guidelines are issued to ensure that future rainwater systems are properly constructed to minimise health risks (Danish EPA, 2002A). Grey wastewater from bathrooms and laundry can be used for toilet flushing, laundry and irrigation but special permits are required. Several research projects have been initiated to form the basis of future legislation (Danish EPA, 2002B).

1.2. CHEMICALS IN THE TECHNOSPHERE

We humans and our environment are exposed to thousands of chemical compounds in our daily life. In the European Union, there are over 102,800 compounds on the market and of these about 30,000 are "everyday" chemicals i.e. estimated to be used in volumes over 1 ton each year (Commission of the European Community, 2001). Furthermore, it has been estimated that 70,000 constituents, including trace elements, metals and XOCs may potentially be hazardous (from Commission of the European Community, 2001). Pharmaceuticals, household chemicals, personal care products, clothing, foodstuffs and additives; building materials e.g. plasticizers and paints; cars, industry, combustion, and incineration are a few examples of the sources of chemical compounds in our environment.

A **xenobiotic** is a compound foreign to an organism, from the Greek word xenos = foreign (IUPAC, 1998). XOCs have come to denote manmade organic chemicals; but fragrances, for example, are foreign to humans and should be included in this group as well as natural

compounds produced artificially in large quantities and for example used in chemical products. Not all XOCs are dangerous and not all natural compounds are non-hazardous as some, e.g. natural fragrances, are bioactive.

There are lists of compounds, which are classified as priority pollutants and hazardous substances (see e.g. Danish EPA; 2000B; European Commission, 2001; OSPAR Commission, 2002). These lists are often comprehensive and record a few hundred compounds, which are only a fraction of the compounds that are potentially hazardous.

Furthermore, there are also quality criteria for drinking water in respect of selected pollutants (Danish EPA, 2001; U.S. EPA, 1999) as well as criteria for discharges into receiving waters e.g. streams, lakes and the marine environment (Danish EPA, 1996; OSPAR Commission, 2002).

1.3. RISK ASSESSMENT TERMINOLOGY

The aim of risk assessments of chemical compounds is to supply a foundation for risk management i.e. decision-making on safety measures for usage. Risk assessments produce an evaluation of whether a chemical compound, in a specific environmental compartment, used in a specific way, may have negative effects on the selected target e.g. humans. The environmental risk assessment terminology used in risk assessments of chemical compounds in the EU for new and existing chemical compounds (European Commission, 2002) is illustrated in Figure 2. The risk assessment is composed of four elements: hazard identification, effects assessment, exposure assessment and risk characterisation. The cycle illustrates that risk assessment is not a linear process but that iterations between the four steps are necessary depending on the problem in focus and the data available.

In general, hazard identification serves to map the inherent properties of chemical compounds by collecting and comparing relevant data, for example on physical state, volatility, mobility, potential for degradation, bioaccumulation and toxicity. The data found is used to identify any negative effect that the compound might have. The effects assessment estimates the dose-response correlation by calculations of predicted no-effect concentrations (PNECs) whereas the exposure assessment includes measurements and calculations of the predicted environmental concentrations (PECs). Comprehensive model systems have been developed to assess the distribution of contaminants in different environmental compartments and in tissue (animals, humans) (see e.g. European Commission, 2002; U.S. EPA, 2000 etc). The next step is risk characterisation, where the potential negative effects are evaluated; and, if possible, the probable incidence of effects is estimated as well the frequency and severity of the negative effects on humans or the environment due to exposure to the compound.

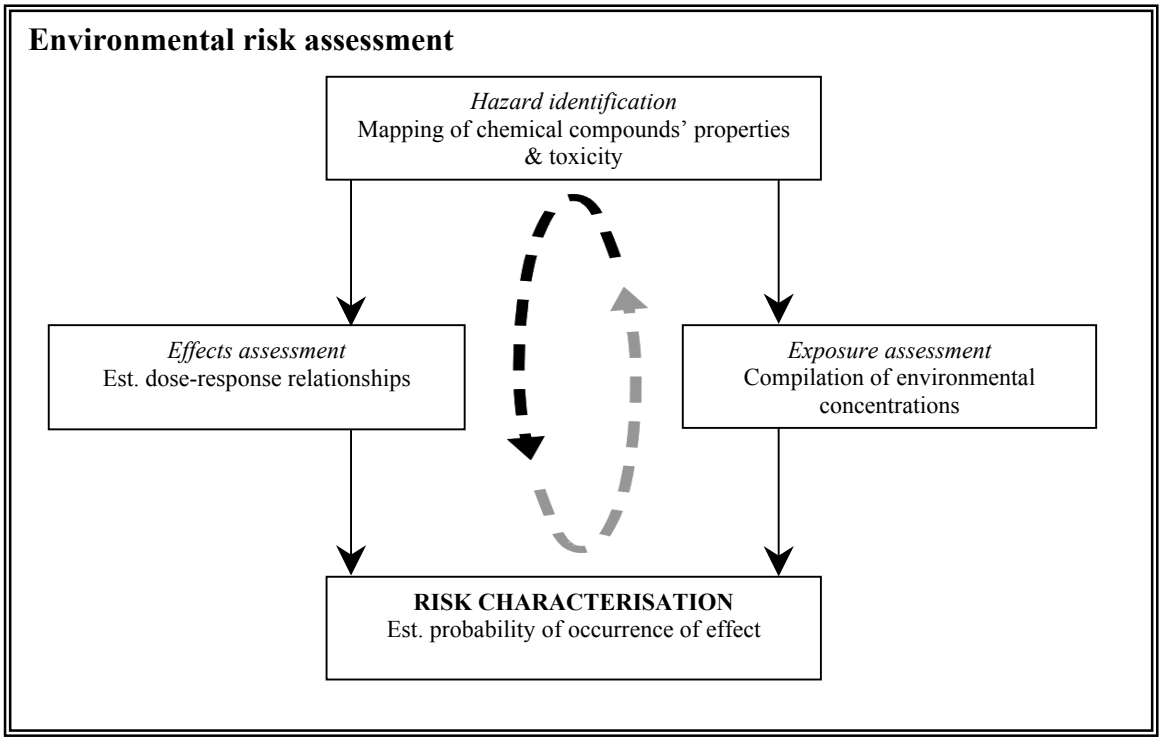

Figure 2. Terminology used in environmental risk assessment of chemical substances (European Commission, 2002).

2. OBJECTIVES

The objective of this PhD study was to develop a methodology for identifying compounds, notably XOCs that might pose a threat in connection with the use of non-potable water in domestic applications or discharge into the environment.

The method has been tested on two different cases: reuse and discharge of grey wastewater and collected rainwater. The domestic applications chosen for the evaluation are toilet flushing, laundry wash, wash of cars and windows as well as discharge into receiving water or soil by e.g. infiltration or irrigation.

The microorganisms of faecal origin are of particular interest in connection with reuse as they represent a potential health risk. These microorganisms may enter the grey wastewater following the washing of hands after toilet visits, bathing of babies and small children after nappy changing etc. and in collected rainwater due to e.g. faeces from bird, foxes, dogs etc. Not only bacteria but also viruses and parasites e.g. *Giardia* and *Cryptosporidium* may be present. *Legionella* may be spread in aerosols and there is a potential risk of microbiological growth within the collection and reuse system. The problems connected with microbiology are not addressed in this thesis although the presence of such problems is alluded to in some of the papers. For more information see other scientists working in this field (Albrechtsen, 1998; Rose *et al*., 1991, Casanova *et al*., 2001A&B; Dixon *et al*., 1999A&B). A large number of microorganisms have been analysed in both grey wastewater and collected rainwater and the survival of some type of organisms in grey wastewater has been found but no re-growth (Albrechtsen, 1998; Rose *et al*., 1991). For a hazard identification of microbiological constituents in collected rainwater see Ledin *et al*. (2002A); while the health risks of microorganisms in grey wastewater reuse have been outlined by a hazard identification and a risk assessment elsewhere (Dixon *et al*., 1999A).

3. METHODOLOGY

The potential problems related to the presence of XOCs in water intended for reuse were examined using the methodology illustrated in Table 1 and Figure 3. It consists of a number of different methods: research of literature and empirical data including chemical analyses; specially developed analytical methods, qualitative measurements of the sources, toxicity measurements and risk assessments, all of which were applied to the two selected cases of reuse of grey wastewater and collected rainwater.

Table 1. Methods used to identify any risk represented by XOCs in water reclamation

Issue	Method		Case: grey waste water	Case: collected rain water	Chapter no.	Paper no.
State-of-the-art	Study of literature on known characteristics		**X**	**X**	**4.1**	**I, II**
Potential sources and their contribution	Study of literature on potential sources and their contribution of pollutants		**X**	**X**	**4.2**	**I, VI**
	Empirical study of sources		**X**	**-**	**4.2.1.2**	**III**
Compounds present	Chemical characterisation	Quantitative analyses	**X**	**X**	**4.3.1**	**III**
		Qualitative analyses	**X**	**-**	**4.3.2**	**III**
	Development of analytical methods	Quantitative analyses	**X**		**4.3**	**IV**
Toxicity	Study of literature on toxicity		**X**	**X**	**4.1, 4.4.1**	**II, VII**
	Toxicity measurements	Test on an algae and	**X**	**-**	**4.4.2**	**VII**
		a terrestrial plant	**X**	**X**	**4.4.3**	**VII**
Potential risk	Study of literature on inherent properties of the potentially present pollutants		**X**	**X**	**-**	
	Risk assessment	Hazard identification	**X**	**X**	**5.2.1, 5.3.1**	**V, VI**
		Exposure assessment	**X**	**-**	**5.2.2, 5.3.2**	**V**
		Effects assessment	**X**	**-**	**5.2.3, 5.3.3**	**V**
		Risk characterisation	**X**	**-**	**5.2.4, 5.3.4**	**V**

X indicates that the method has been applied to the selected case.

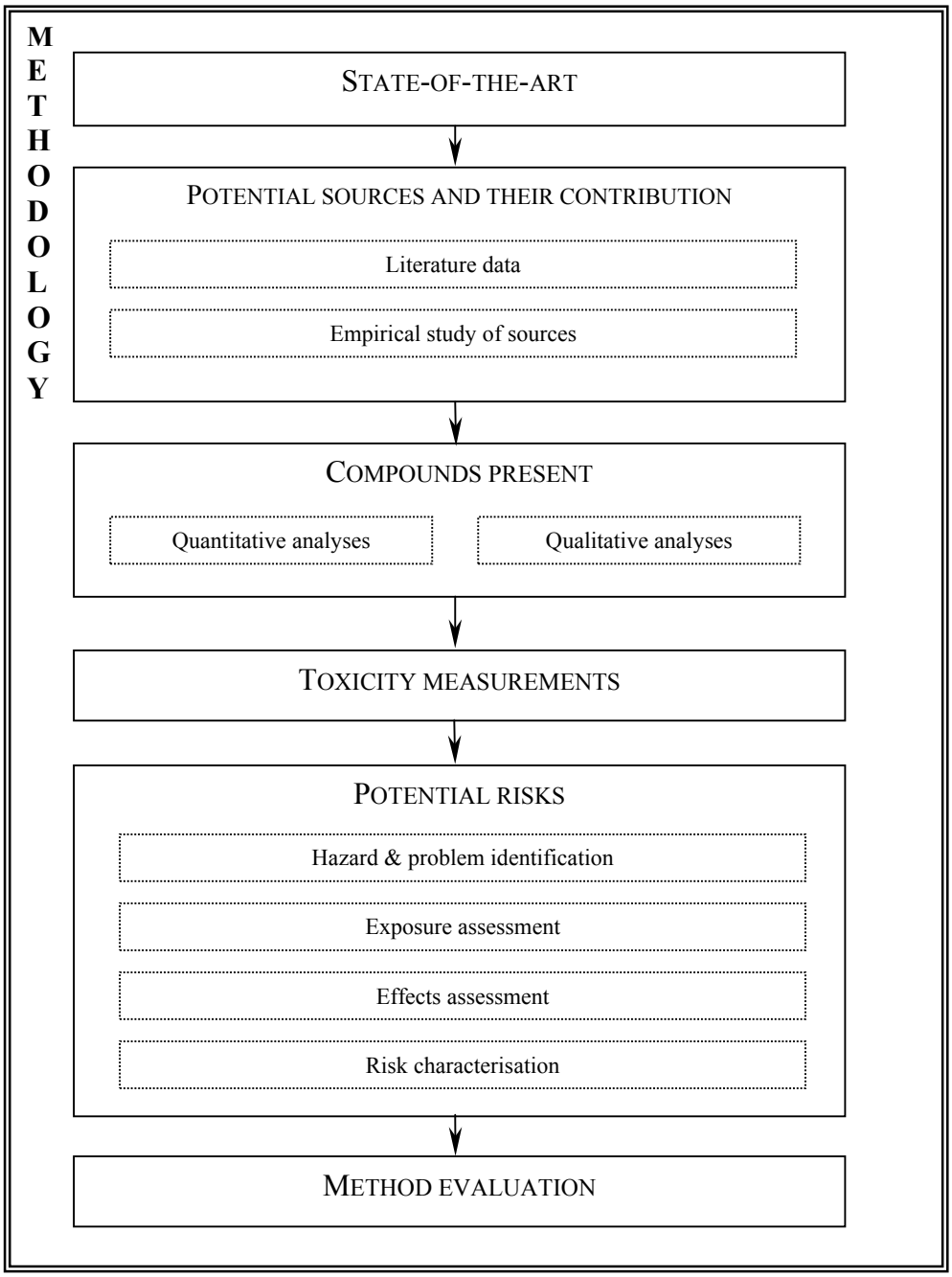

Figure 3. Methodology used to establish whether XOCs present a risk in water reclamation, illustrated as a flow diagram.

Sampling of grey wastewater was done primarily at BO90, a tenant-owned development in the central part of Copenhagen (Denmark), where grey wastewater from bathrooms (handbasins, showers and bathtubs) is collected and treated on-site to be reused for flushing toilets (***Paper III, IV, VII***).

4. COMPOUNDS, SOURCES AND CONCENTRATION LEVELS

4.1. IDENTIFIED AND POTENTIALLY PRESENT COMPOUNDS

Information regarding pollutants (physical, chemical, microbiological constituents as well as toxicity data) present in grey wastewater and collected rainwater was gathered by researching published international literature (articles, conference proceedings, official reports etc).

Observations and measurements of different types of constituents in these water fractions were researched: covering the period of 1970 to 2001 for grey wastewater, and 1980 to 2001 for collected rainwater and run-off (***Papers I and II***). In the case of grey wastewater, this research was extended by 10 years due to the limited material found. The time span was restricted as changed legislation, e.g. the ban on lead in petrol and the ban on phosphorous in detergents has changed the compounds that could be present. Moreover, new analytical methods with improved sensitivity can detect compounds, which were not previously thought to be present.

Data on household and municipal wastewater was also gathered by way of supporting evidence since compounds in the wastewater could also be present in grey wastewater. Deposition data (wet and dry) was studied as these fractions make up a part of the load in the collected rainwater fractions.

4.1.1. Grey wastewater

The compounds present in grey wastewater vary from household to household, where the lifestyles, customs, installations and use of household chemical products will be of importance. Furthermore, the characteristics will differ between the different grey wastewater sources within a household (***Paper I*** and references therein). The composition will vary significantly in terms of both time and place due to the variations in water consumption relative to the discharged amounts of compounds. Furthermore, chemical and biological degradation of the chemical compounds will occur within the sewage system and during storage.

It was found that existing studies of the composition of grey wastewater investigated mainly the physical and chemical constituents and focussed on organic matter such as BOD and COD and nutrients (N, P) as well as the presence of microorganisms (***Paper I***). A few investigations of the metal content were found but no information regarding the presence of individual XOCs. Detergents and long-chain fatty acids were detected in investigations of mixed grey wastewater and shower wastewater; however, no concentrations were measured (Santala *et al*., 1998; Burrows *et al*., 1991). In recent material the focus has been on the presence of XOCs (Palmquist and Hanæus, 2001, and ***Paper III***, ***Paper IV***). In the study of Palmquist and Hanæus (2001), of the 85 XOCs tested for, 49 were detected. The number of constituents found to have been observed or quantified in grey wastewater (excluding this Ph.D. study) is given in Table 2.

Table 2. Constituents, which according to available literature are to be observed/quantified in grey wastewater (Data from *Paper I* and *VII,* Palmquist and Hanæus, 2001, Casanova *et al*., 2001A&B).

Type of constituents	Number of constituents
Physical constituents	14
Chemical constituents	21
Metals and inorganic trace elements	27
Xenobiotic organic compounds	87
Microbiological constituents	19
Toxicity data	3
Total	**172**

The impact of storage on grey wastewater has been investigated and it was found that storage for 24 hours improved the quality of the water but storage for more than 48 hours could be a serious problem due to depletion of the dissolved oxygen (Dixon *et al*., 1999B). No microorganism growth was observed but it was found that microorganisms can prevail in the grey wastewater system for some time (Albrechtsen, 1998; Rose *et al*., 1991).

4.1.2. Collected rainwater

The literature researched on observations and measurements of constituents in urban run-off and collected rainwater clearly illustrates that there are a large number of constituents that have been identified and quantified. In total, 603 different physical, chemical and microbiological constituents and toxicity were found; see Table 3.

Table 3. Constituents that have been observed/quantified in collected rainwater (*Paper II*).

Type of constituents	Number of constituents
Physical constituents	30
Chemical constituents	75
Metals and inorganic trace elements	78
Xenobiotic organic compounds	385
Microbiological constituents	22
Toxicity data	13 studies
Total	**603**

Most studies were performed on the catchment types: roads, roofs and urban areas. The dominating constituents for the analysis were the physical and chemical constituents, metals as well as the polycyclic aromatic hydrocarbons (PAHs) and the pesticides among the XOCs.

Two large studies of XOCs in run-off were found: one from the USA where 106 compounds were tested for and 63 were observed (Cole *et al*., 1984); the other was from Denmark, where 71 compounds were analysed for and 49 observed (Kjølholt *et al*., 1997). Generally, polycyclic aromatic hydrocarbons (PAHs) and pesticides are the most examined XOCs while the majority of the other compound groups only were analysed for in one single study.

For the most intensively studied compounds (metals, PAHs and organic summary constituents) the speciation, i.e. the distribution between the dissolved and the particulate phases, as well as the distribution between different dissolved species have been measured. Some of the metals have been divided according to size to get an idea of amounts in particulate form compared with amounts in dissolved form and the distribution of compounds in the different range of sizes. This gives information e.g. on mobility and bioavailability of the metals. For example, lead and zinc will appear in different phases: Pb primarily in the particulate faze whereas Zn can mainly be found in a dissolved state (Ledin *et al*., 2002A).

It was found in the literature researched as well as in studies of CSOs, for example, that the concentration levels of the compounds vary significantly both within one rain event, between events at one site and between sites. For example the first flush effect has the implication that the concentration of compounds is higher at the beginning of a rain event that later in the same event. This can be explained partly by the fact that compounds accumulate in the atmosphere or on the surface during dry weather and are subsequently washed out in high levels at the beginning of an event, but as the source is emptied, the concentration levels drop. Time delay, sedimentation, re-suspension and corrosion of piping material can level out the effects (see e.g. Arnbjerg-Nielsen *et al*., 2000) and the opposite effect of low compound concentrations at the start of one event has also been observed, which may be explained by slow leaching of compounds from roofing materials, for example. This demonstrates that there may be a great difference, within the time scale, between the concentrations of different compounds between rain events at the same catchment site (Ledin *et al*., 2002A).

4.2. POTENTIAL SOURCES AND THEIR CONTRIBUTION

The literature was also studied for constituents that could potentially be present in grey wastewater and collected rainwater due, for example, to contact with surfaces or a human activity (consumption of detergents, car driving, weed spraying, etc.).

The characteristics of grey wastewater depend firstly on the quality of the water supply; secondly on the type of distribution network for both the drinking water and the grey wastewater i.e. leaching from piping, chemical and biological processes in the distribution network; and thirdly on the activities within the households. Declarations of contents of common Danish household products, consumption statistics and consumer databases were researched for information on compounds in these sources (***Paper I***; Ledin *et al*., 2002B). In the specific case study, at BO90, the information from the local waterworks was acquired and the material in the piping examined.

Four major sources of compounds in collected rainwater were identified: atmospheric deposition, releases from solid materials, human activities and animal activities. Some of the sources, e.g. “releases from materials”, were divided into subgroups: buildings, roads and cars, etc. The international literature and material databases were searched for information regarding the presence of constituents that could be released from these sources and thereby potentially contribute to the load of compounds in collected rainwater; for more details see ***Paper VI*** and Ledin, *et al*. (2002A) and references therein.

A one-week empirical study of the consumption of household chemicals and personal care products was carried out at BO90 (***Paper III***). The inventory was made using interviews, questionnaires and a record of products. The inhabitants were asked to record on diary sheets each activity that led to grey wastewater production in the bathrooms. They were also asked to deliver all households and personal care products they use in their bathrooms; the products were recorded by name, manufacturer, declaration of contents and weight (for more details see ***Paper III*** and Ledin *et al*., 2002B). It was, however, not possible to assess the amount of the compounds using the declaration of contents since that information is not given on the labels. Furthermore, only compounds present in levels of above 1% are required to be listed (Danish EPA, 2000A), which means that compounds present in relatively low concentrations will not appear on the declaration of contents. In addition, impurities in the raw material used, in help-compounds used in production and in compounds used as solvents for perfumes and aromatics are not required to be listed on the labels. Fragrances and flavours as well as aromatics are only required to be declared as “perfume” and “aroma” (Danish EPA, 2000A).

4.2.1. Grey wastewater

4.2.1.1. Literature

The XOCs that could be expected to be present in grey wastewater constitute a heterogeneous group of compounds that originate from the household chemicals and personal care products such as detergents, soaps, shampoos, perfumes, dyes and cleaning products. The kitchen wastewater contains lipids (fats and oils); tea, coffee, soluble starch, diary products and glucose, while the wastewater produced from laundry will contain different types of detergents, bleaches and perfumes, for example. Based on information available in the declaration of contents in different types of common Danish household products, at least 900 different organic chemical compounds and compound groups can be listed (***Paper I***). However, this is only a fraction of the actual number of compounds present, as compounds present <1% in the products are not required to be listed on the declaration of contents (Danish EPA, 2000A). The major compounds listed are the surfactants used in detergents, dishwashing liquids and hygiene products i.e. non-ionic, anionic and amphoteric surfactants. Other large groups are the fragrances and flavours, the solvents and the preservatives. Preservatives are added to the vast majority of household chemicals to prevent microbiological growth in the product and since they are biocides and fungicides, are they toxic in some concentrations. By-products can be formed when different chemical compounds in grey wastewater react with each other and oxidation as well as microbiological activity can lead to the production of degradation products that may have other properties than the parent compounds (see e.g. the Swedish EPA, 1992).

4.2.1.2. Empirical study of sources – Inventory of BO90

In the inventory made in the case study at BO90 during one week of a four-week water-sampling programme, the consumption of household chemicals and the contents of the chemicals were investigated.

The diary survey of water-consuming activities, the inventory of the consumption of household chemicals and the recording of the lists of contents of the household chemicals resulted in over 90 individual products, which were recorded and weighed in the product list. The dominating products (in number of bottles) were shampoo, soap, oral hygiene products, hair conditioner and skin creams (***Paper III***).

During the inventory week, 1100 g of household chemicals were used in the bathrooms in 11 out of the 17 flats, which corresponds to about 40 g per person per week. The three most frequently used products - shampoos, soaps, and oral hygiene products – accounted for 66 % of the total consumption. According to the declarations of contents on the products recorded 290 different organic and inorganic constituents were present; of these, 237 were organic compounds: 53 surfactants, 26 emulsifiers, 47 fragrances and flavours, 20 preservatives and antioxidants, 3 softeners and plasticizers, 4 UV-filters, 10 solvents, 11 dyes and 61 miscellaneous compounds. By far the most extensively utilised constituents were glycerine, citric acid and perfume; each was recorded in more than 30 products. It was noted that among the 290 constituents, 48 contained sodium, not only as an inorganic salt but also as the counter ion to an organic acid (***Paper III***; Ledin *et al*., 2002B).

The result shows that not all tenants delivered all their personal care products used during the inventory week since no cosmetics, for example (lipstick or mascara etc.), were reported to be in use although 47% of the adult inhabitants were women (Ledin *et al*., 2002B).

The overlap between the 900 organic compounds found in the literature researched and the 237 XOCs found in the inventory were 94 compounds. There was, however, a large number of compounds that were relatively unspecified e.g. fragrances, aroma and perfume.

4.2.2. Collected rainwater

The four major sources of constituents in collected rainwater: atmospheric deposition, releases from materials, human activities and animal activities were investigated for the compounds which they could contribute to the load of constituents in collected rainwater (for more details see ***Paper VI***; Ledin, *et al*., 2002A and reference therein).
Examples of sources that leach, corrode, erode and emit compounds into the surrounding environment are cars e.g. brakes, tyres, exhaust fumes, windscreen washer fluids, petrol and oils, crankcase oils, antifreeze mixtures, and brake fluids etc. Human activities include the spreading of pesticides, road salts and fire-extinguishing agents as well as accidental spillage. Construction materials used in houses, roads, gutters, etc. may all leach compounds as they are washed by rain during a rain event.

Seventeen metals and 337 XOCs were identified as potentially present from the potential sources. However, it should be mentioned that the research of potential sources carried out within the project was limited, due to a restricted timeframe (for more details see Ledin, *et al*., 2002A) and therefore the number of constituents that might be present would probably increase if the research were extended.

There was a relatively limited number of constituents that belonged to both groups, i.e. constituents that have been identified in collected rainwater and pointed out as potentially present (Table 4). This observation indicates that although a large number of inorganic and organic constituents have been found in collected rainwater, there could be at least as many constituents present for which no-one has yet tried to analyse (***Paper VI***).

Table 4. Number of compounds that have been identified in collected rainwater; number of potentially present compounds; and number that have been found in both categories.

Compound group	Compounds identified in collected rainwater	Potentially present compounds	Number of compounds present in both categories
Metals and inorganic trace elements	*27*	*17*	*14*
Xenobiotic organic compounds			
Aliphatic amines	*0*	*6*	*0*
Alkanes	*18*	*42*	*17*
Aromatic hydrocarbons	*7*	*18*	*4*
Chlorophenyls	*0*	*1*	*0*
Dioxins and furans	*34*	*8*	*5*
Ethers	*8*	*7*	*2*
Halogenated aliphatic hydrocarbons	*27*	*27*	*17*
Halogenated aromatic hydrocarbons	*12*	*25*	*6*
Organolead compounds	*9*	*0*	*0*
Organotin compounds	*0*	*9*	*0*
PCBs	*14*	*0*	*0*
Pesticides	*118*	*63*	*17*
Phenols	*27*	*36*	*20*
Phthalates and adipates	*8*	*8*	*6*
Polycylic aromatic hydrocarbons (PAHs)	*45*	*25*	*25*
P-triesters	*3*	*2*	*2*
Miscellaneous	*25*	*60*	*2*
Total	***382***	***354***	***137***

4.3. CHEMICAL CHARACTERISATION

The chemical analyses consist of quantitative analyses of selected constituents and qualitative screening for XOCs. The chemical characterisation has been done by the methods presented in Table 5.

Table 5. Analysis methods used for the chemical analyses

Analytical parameters	Method reference
Physical constituents	Danish Standard Methods and com. accredited analyses
General chemical constituents	Danish Standard Methods and com. accredited analyses
BTEX	Environment & Research DTU, 2002A
Drugs	Hovvang, 2002 (from Moeder *et al*., 2000 and Majzik-Solymos *et al*., 2001)
Long-chain fatty acids	***Paper IV***
Metals and trace elements	Commercial accredited analyses
Nonyl phenol carboxylates	Field and Reed, 1996
Screening for XOCs	Paxéus and Schröder, 1996 and ***Paper III***
Selected XOCs	Commercial accredited analyses
Microbiological constituents	Commercial accredited analyses

Quantitative analyses of selected constituents in raw grey wastewater in case study at BO90 consisted of 4 physical and 12 chemical constituents, 23 metals and trace elements, 65 XOCs and 12 microbiological constituents and were made by accredited commercial laboratories

(SGAB Analytica, Sweden and Rovesta Miljø I/S, Denmark) or at the laboratory of E&R DTU, according to Danish Standard Methods. Samples were taken daily for four weeks at the inlet of the treatment facility and were the first part of a grey wastewater-monitoring programme financed by the Danish EPA (Ledin *et al*., 2002B).
Additional analyses of XOCs in grey wastewater from BO90 during the period 2000-2002 were made by methods developed at the E&R DTU and published in international literature. These analyses include 20 BTEXN, 9 long-chain fatty acids and caffeine, paracetamol and ibuprofen as well as the nonyl phenol carboxylates (NP1EC and NP2EC) (E&R DTU, 2002A; ***Paper IV***; Hovvang, 2002; Field and Reed, 1996).

No quantitative analyses of collected rainwater were conducted within this project.

A qualitative screening for XOCs in grey wastewater from BO90 was performed, based on a procedure used to screen non-regulated compounds in wastewater (Paxéus and Schröder, 1996). The analyses included solid phase extraction with four different solid phases, after which the extracts were analysed by GC-MS. Identification of experimentally found compounds was based on material from reference libraries, spectra' published in the literature and commercial reference compounds (***Paper III***).

Motorway run-off from Albertslund motorway (Denmark) was screened for XOCs in accordance with the strategy set out in ***Paper III*** but the study was restricted to use two solid phases for extraction (Jensen, 2002).

4.3.1. Quantitative analyses of grey wastewater

Chemical analyses were primarily performed on samples from the case study at BO90. Part of the data is presented in Table 6 (***Paper III***; Ledin *et al*., 2002B; Hovvang, 2002).

Table 6. Chemical characteristics of mixed bathroom grey wastewater (BO90) compared with other studies.

	Bathroom ww[A] BO90 17 households	Bathroom ww[B] Literature data	Mixed grey ww[C] 47 households	Mixed grey ww[D] 12 households
Physical constituents (in mg/L)				
Temperature (°C)	18.3-31.1	29		
Electric conductivity (µS/cm)	613-1890	82-250		360-520
Suspended solids	7-207	40-120		
Chemical constituents (in mg/L)				
pH	7.2-8.6	6.4-8.1	6.06-8.38	6.87-8.15
BOD_5	18.6-286	76-200		41.0-85.0
BOD_7	26-130	50-300	350-500	
COD	46-271	100-633	495-623	
Tot-N	3.2-46.4	5-17	8-11	
Tot-P	0.28-4.2	0.11-2	4.6-11	
Alkalinity (meq/L)	5.4-13.5	24-67 ($CaCO_3$)		
Chloride	50.7-88.0	9.0-18		16.3-33.4
Sulphate	52-97	-		39.8-88.5
Metals and trace elements (in µg/L)				
Al	205-925	<1000	1480-3390	
Ba	34-43		15.5-21.8	
Ca	95900-99600	3500-7900	31600-38000	
Cd	0.056-0.66	<10	0.0627-0.16	
Cu	18.6-84.3	60-120	47-70.2	
Fe	79-341	340-1100	175-567	
K	5860-7390	1500-5200	7690-8850	
Mg	20800-23000	1400-2300	5300-6220	
Mn	8.81-14.5		9.55-14.3	
Zn	203-761	60-6300	55.3-77.8	

XOCs (in µg/L)			
Alkylphenols			
Nonylphenol	< 0.5		2.82-5.95
Nonylphenol ethoxylates	< 5		86-228
Octylphenol	< 0.25		0.081-0.156
Octylphenol ethoxylates	< 3		2.1-12.7
BTEXN			
Benzene	< 1.9		< 1.0
Ethyl benzene	1.9-2.1		< 1.0
Naphthalene	< 4.5		< 5.0
Xylenes	3.9-4.3		< 1.0
Toluene	1.3-1.6		< 1.0-1.9
Fatty acids			
Long-chain fatty acids	< 0.5-27100	Detected	
Miscellaneous			
Triclosan	0.6		0.56-5.9
Phthalates			
Butyl benzyl phthalate	< 1		< 1.0-9
DEHP	11-39		8.4-160
Di-cyclohexyl phthalate	< 1		< 1.0
Di-isobutyl phthalate	< 1-3		< 1.0-8
Di-n-butyl phthalate	< 1		1.8-9.2
Di-n-propyl phthalate	< 1		< 1.0
Dipentyl phthalate	< 1-1.4		< 2.0
Diethyl phthalate	< 1-13		4.2-38
Dimethyl phthalate	< 1		< 1.0
Microorganisms (per 100 mL)			
Aeromonas	40-5100		
Campylobacter sp.	nd	nd	
Clostridium perfringens	3-15		
Cryptosporidia		nd	nd
E. Coli	$<1\text{-}4\times10^5$		$3.2\text{-}3\times10^2$
Enterococci	$1.0\times10^3\text{-}7\times10^3$		
Faecal coliforms		$32\text{-}6\times10^3$	$6.4\times10^2\text{-}8.6\times10^6$
Faecal Streptococci		$1\text{-}7\times10^4$	$8\text{-}9\times10^2$
Giardia		nd	nd
Haemolytic bacteria	1.7×10^3		
Pseudomonas aeruginosa	$10\text{-}8.7\times10^3$	nd	$2\times10^2\text{-}1.6\times10^5$
Salmonella sp.	nd	nd	
Staphylococcus aureus		$<1\text{-}5\times10^3$	nd
Total bacterial pop.	$9.1\times10^4\text{-}5.1\times10^9$	$107\text{-}3\times10^8$	
Total coliforms	$1.1\times10^3\text{-}1.6\times10^9$	$105\text{-}2.4\times10^7$	$6.6\times10^5\text{-}2.1\times10^8$

[A]Ledin *et al*., 2002B (BO90 with 17 households, up to 160 samples per constituent)
[B]***Paper I*** (8 studies of bathroom ww.)
[C]Palmquist and Hanæus, 2001 (4 samples of mixed grey ww from 47 households)
[D]Casanova *et al*., 2001A & B (Mixed grey ww from 12 households)

The levels of organic matter, nutrients and microorganisms found at BO90 does not deviate significantly from grey wastewater data found in the literature, however all constituents have not been analysed in other studies so no comparisons can be made. The metal concentrations found at BO90 are in the same range as have been found in other studies except for the alkali and alkali earth metals, which are higher at BO90 due to the high levels, found in the potable water (***Paper III***).

A few representative constituents from the major groups of detergents were included i.e. anionic, cationic and non-ionic detergents. The anionic detergent LAS was found to be present in the range of <25-450 µg/L, cationic detergents were found in the range of <100-2100 µg/L while the non-ionic detergents nonylphenol and octylphenol ethoxylates were all below the limit of detection (***Paper III***) as were their aerobic degradation products, nonylphenol carboxylates (NPE1C and NPE2C) (Hovvang, 2002). The cationic detergent in this grey wastewater derives predominantly from hair conditioners and not from fabric softeners, which are otherwise a major source of cationic detergents in household wastewater,

as the laundry water is diverted to the municipal treatment plant. Low levels of the volatile toluene, ethyl benzene, and xylenes were found as were done by Palmquist and Hanæus (2001) (Table 6). Seventeen chlorophenols were included in the analyses. Most of these were below the detection limit but 2,4- and 2,5-dichlorophenol were present at 0.06-0.13 µg/L and 2,4,6-trichlorophenol ranged between <0.02-0.10 µg/L whereas the concentration of pentachlorophenol (PCP) ranged between <0.02-0.04 µg/L. The chlorophenols are mainly used as preservatives (***Paper III***; Ledin *et al*., 2002B). For the other compounds no data for comparison were found.

Even-numbered long-chain fatty acids (C_6 to C_{20}) were found in the range of <0.5-27100 µg/L (***Paper IV***). They have not previously been quantified in grey wastewater, but have been detected in a GC-MS screening of shower wastewater from a military facility (Burrows *et al*., 1991), see Table 6. In the grey wastewater samples, several other fatty acids were also found to be present. The straight chains of the small C_4-C_5, the uneven C_{11} to C_{17} and the long-chain C_{22} and C_{24} were identified. A number of mono-unsaturated compounds of C_{16} and mono and di-unsaturated chains C_{18} were also present as well as a few branched chains of different sizes.

4.3.2. Qualitative and semi-quantitative analyses of grey wastewater

One hundred and ninety one (191) different XOCs were identified in the extracts of grey wastewater from BO90 in the qualitative screening. Half of the compounds identified were long-chain fatty acids and their esters e.g. methyl-, hexadecyl- and octadecyl-esters. Both nonyl and octylphenols were present in the grey wastewater, but none of the ethoxylates was found (***Paper III***). The group of alkyl phenols include several compounds that have come into focus because nonylphenol is an endocrine disrupter i.e. male and female reproductive toxicant (NTP, 2001). Nonylphenol is used as a cleaning agent, softener and stabiliser but as an intermediate in the industrial processes (IUCLID, 2000). It can also be formed by anaerobic degradation of the non-ionic detergent nonylphenol ethoxylates (Ahel *et al*., 1994). Here octyl and nonylphenol were semi-quantitatively assessed at 0.2 and 0.4 µg/L, respectively.

More than 40 fragrances and flavours were identified e.g. citronellol, coumarin, eucalyptol, hexyl cinnamic aldehyde and menthol (***Paper III***). This group is present as perfume additives in personal care products or as flavouring e.g. in. toothpaste. Caffeine is present in coffee, tea, and some soft drinks and was found in the screening at 0.5 µg/L and in the quantitative analyses <5.8 µg/L (***Paper III***; Hovvang, 2002).

The group "preservatives" consists of preservatives and antioxidants and among them butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) were found (***Paper III***). These substituted phenols are widely used as antioxidants and added to plastic materials and petroleum products. BHT is also used as a food additive and as an antioxidant in food packaging and soaps as well as anti-skinning agent in paints and inks (HSDB, 2002). Here, BHT and BHA were present at 4.5 and 0.5 µg/L, respectively.

Observed preservatives included ethyl and methyl paraben, citric acid and phenoxy acetic acid as well as triclosan. Triclosan is used as an antiseptic in a vast array of consumer products e.g. as odour-eaters in shoes and as an antibacterial agent in toothpaste (Daughton and Ternes, 1999). The semi-quantification indicates that triclosan was present at 0.6 µg/L, which correlates well with the levels found in grey wastewater from Sweden: 0.56-5.9 µg/L (Palmquist and Hanæus, 2001) (Table 6). The parabens are one of the most widely used types of antimicrobial preservatives in cosmetics, toiletries, detergents, pharmaceuticals and foods (Acme-Hardesty, 2001). One pesticide was found to be present: malathion, which is used as the active ingredient in lice shampoos and can be purchased in Danish pharmacies.

In all samples, nine softeners and plasticizers were found: the phthalates, bis(2-ethylhexyl)- (DEPH), dibutyl-, diethyl-, dimethyl and mono ethylhexyl phthalate, dominate this group. Two other plasticizers similar to DEPH in structure were identified as well as di-(ethylhexyl) adipate (diester of hexanedioic acid) and di-(ethylhexyl) sebacate (diester of decanedioic acid). DEHP was present at 10 µg/L, whereas the other two diesters were found in the concentrations of 1 µg/L each. All other phthalates were present in the concentrations <10 µg/L in the screening. The methyl ester of hexadecanoic acid was found to be present at 14.2 µg/L (***Paper III***).

By way of comparison with the phthalates and concentration levels found by Palmquist and Hanæus (2002) in unspecified Swedish grey wastewater, it was found that diethyl phthalate, di-isobutyl phthalate and DEHP were present in both studies whereas butyl benzyl phthalate and di-n-butyl phthalate were present in the study by Palmquist and Hanæus but not at BO90 (Table 6).

It can also be noted that several miscellaneous compounds, which probably do not derive directly from household chemicals, were identified e.g. medicinal residuals, flame-retardants, as well as the drug nicotine. Medicinal and drug residuals can be explained by excretion from human bodies during showering, tooth brushing and washing (present in the mouth or on the skin or excreted by urination). The medicinal acetaminophen (paracetamol) is an analgesic and anti-inflammatory agent and is used in common painkillers. The phosphorous compounds are esters of phosphoric acid and are used as flame-retardants. Tri(2-chloroethyl) phosphate and triphenyl phosphate were detected and they had most likely rubbed onto the skin from clothes and washed off during showering. The presence of cholesterol and coprostanol as well as other faecal sterols indicate some faecal contamination of the grey wastewater (***Paper III***).

In a comparison with another grey wastewater, a WWTP in and effluent, and with contaminated river water, a number of compounds were the same and the concentration levels were of the same magnitude (***Paper III***; Palmquist and Hanæus, 2001; Paxéus and Schröder, 1996; Kolpin *et al*., 2002)

Comparison between the compounds found in the inventory, in the semi-quantitative and the quantitative analyses showed that 16 compounds found in the inventory were also identified in the semi-quantitative screening e.g. long-chain fatty alcohols and acids, preservatives and fragrances (Table 7). The pesticide malathion found in the semi-quantitative screening were not found on the declaration of contents on the products handed in during the inventory, but by personal communication after the analyses were finalised. One tenant confirmed having used lice shampoo during the sampling period.

One of the reasons for the low overlap between the screening and the inventory is the limitation of the screening, which only allows analysis of thermally stable, non or low charged compounds that can be volatilised for the gas chromatographic analysis. This excludes a large part of the compounds present, for example detergents and softeners, which would have been possible to find if another analysis method had been used e.g. liquid chromatography i.e. the analyses are only a snapshot of what actually are present.

Table 7. Comparison of compounds from the inventory, quantitative and semi-quantitative analyses

Compound	Semi-quantitative analyses (µg/L)#	Quantitative analyses (µg/L)#	Inventory
1-Hexadecanol	63.7		**X**
1-Octadecanol	117		**X**
9-Octadecenoic acid	27.4	144-15863	**X**
Benzoic acid	0.5		**X**
BHT	4.5		**X**
Caffeine	0.5	<5.8	
Camphor	9.1	9.1-11.4	**X**
Citric acid	15		**X**
Decanoic acid	1.2	5.5-755	
DEHP	9.8	11-39	
Diethyl phthalate	4	<1-13	
Dimethyl phthalate	4.9	<1	
Dodecanoic acid	15	5.9-680	**X**
Eicosanoic acid	1.3	19.7-189	
Ethyl benzene	2	1.9-2.1	
Ethyl paraben	0.6		**X**
Hexadecanoic acid	76.9	291-7020	**X**
Isopropyl myristate	1.6		**X**
Malathion	1.9		**X***
Methyl paraben	2.6		**X**
Nonylphenol	0.4	<0.5	
Octadecanoic acid	4.2	31.0-3569	**X**
Octanoic acid	3	8.1-283	
Octylphenol	0.2	<0.25	
Paracetamol	1.5	<5.5	
p-Cresol	3.1	<1	
Salicylic acid	0.6		**X**
Tetradecanoic acid	12.6	44.4-2808	**X**
Toluene	1.4	1.3-1.6	
Triclosan	0.6		**X**
Xylene, m-	3.5	3.4-3.6	
Xylene, o-	0.6	0.5-0.7	

*Confirmed after the inventory

Samples for quantitative and semi-quantitative analyses were sampled during the same day but not at the same time i.e. concentrations differences between the two are expected. Furthermore were samples for quantitative analyses pooled to make weekly samples except for the long-chain fatty acids and BTEX, which were analysed at E&R DTU.

The levels of phthalates (e.g. DEHP and diethyl phthalate) as well as nonyl phenol, caffeine and paracetamol were found in the same concentration range in the screening and in the quantitative analyses (***Paper III***, Hovvang, 2002) whereas the chlorophenols found in the quantitative analyses were not listed the declaration of contents on the household chemicals and personal care products (***Paper III***).

These observations illustrate that an inventory of the use of household chemicals cannot be a substitute for a full characterisation of the compounds actually present in grey wastewater.

The specific content and the individual concentrations will vary during the day and the days of the week as the use of chemicals vary depending on the time of day and day of the week.

4.3.3. Analyses of collected rainwater

Four compounds were identified in the extracts from motorway run-off in a qualitative screening. The compounds were dibutyl phthalate and 3 substituted phenols (2,4-bisdimethylbenzyl phenol, 2,4-bis(dimethylbenzyl)-6-*tert*-butyl-phenol and 2,6-bis(*tert*-butyl)-4-dimethylbenzyl)phenol) (Jensen, 2002). None of these phenols had previously been listed as either found or potentially present.
No quantitative analyses were made of collected rainwater within this PhD thesis except for a few physical and chemical constituents to support the qualitative analyses and toxicity measurements (see Jensen, 2002; Výmetalova, 2001).

4.4. TOXICITY MEASUREMENTS

Toxicity measurements performed in this study include phytotoxicity tests on willow trees and green algae. The environmental risk assessments mainly focus on the individual compounds whereas toxicity tests can be used to test whole sample toxicity i.e. the toxicity that arises from the individual compounds, the matrix and synergistic effects. Toxicity tests can be used as a supplement to the risk assessment. Tests were made in order to see if an actual problem caused by exposure of untreated grey wastewater and collected rainwater could be illustrated, i.e. if the potential risk seen in the risk assessment could be confirmed. The methods used are presented in Table 8 along with the references.

Table 8. Methods used for toxicity measurements

Analytical parameter	Method reference
Algal growth inhibition test	Arensberg *et al*. (1995); Nyholm and Källquist (1989); Mayer *et al*. (1998)
Willow short-term acute assay	Trapp *et al*. (2000)

The phytotoxicity of different grey wastewater fractions was evaluated by testing on aquatic green algae, *Pseudokirchneriella subcapitata* and a terrestrial plant, willow (*Salix scherinii x viminalis var. "Kristina"*) (***Paper VII***). A freshwater aquatic plant and a terrestrial plant were chosen to represent the receiving surface waters and irrigation and/or infiltration into soil. The green algae *P. subcapitata* were found to be more sensitive than a number of other aquatic organisms e.g. bacteria (*Vibro fischeri*) and invertebrates (*Daphnia magna* and *Brachinus calyciflorus*) (Radix *et al*., 2000; Nyholm and Källquist, 1989) whereas the willow trees are relatively insensitive and are used for phytoremediation of contaminated soil and for treatment of landfill leachate and wastewater (Trapp *et al*., 2000; Aronsson and Bergström, 2001; Stubsgaard, 2001).

In addition, willow phytotoxicity tests were performed on a number of different grey wastewater fractions along with two roof run-off samples and one surface run-off sample (Výmetalova, 2001).

4.4.1. Literature data

The phytotoxicity of artificial and genuine grey wastewater has been examined in three studies for wheat, lettuce, and soybean root-associated bacteria (Garland *et al*., 2000; Kerkhof *et al*., 2000; Wigharajah and Bubenheim, 1997). The surfactant content of the grey wastewater was found to cause growth inhibition in lettuce but not in wheat and to cause changes in the rhizosphere communities. The surfactant used in these tests was the anionic Igepon which suppressed the fresh weight production of lettuce by 40 % when exposed to concentrations similar to what could be found in grey wastewater (250 mg/L); i.e. direct

utilisation in crop irrigation would be a problem due to the presence of detergents (Wigharajah and Bubenheim, 1997).

Thirteen investigations that concern the toxicity of collected rainwater from impervious urban areas were found. The toxicity was measured as aquatic toxicity by tests on a number of fresh water organisms such as fish, crustaceans and algae but a few investigations of tests with saltwater organisms were also found (Ledin *et al*., 2002A). However, a large number of investigations focussing on the effects in the recipient were also found and in all these studies, all analyses had been made downstream of the outflow of motorway run-off, for example. This type of toxicity test, i.e. diluted by recipient water, has been outlined in other articles and reviews (see e.g. Oberst *et al*., 2000; Burton Jr *et al*., 2000; Tucker *et al*., 1999; etc).

4.4.2. Algae growth inhibition tests

Tests of growth inhibition of the green algae *P. subcapitata* were made with several types of grey wastewater (mixed bathroom, shower, handbasin, laundry and kitchen sink). Filtrated samples yielded a 50% effect concentration (EC_{50}) 100->1000 mL/L (Table 9).

Table 9. Effect concentration (EC_{50}) for *P. subcapitata* exposed to different types of grey wastewater (*Paper VII*). Expressed as 95% confidence interval: average [min; max].

Sample	EC_{50} (mL/L)
Bathroom grey wastewater	
BO90 (mixed)	949 [623; 1450*]$_{95\%}$
Nordhavnsgården (mixed)	726 [610; 864]$_{95\%}$
Handbasin ww.	1200* [950; 1530*]$_{95\%}$
Shower ww.	141 [74.2; 268]$_{95\%}$
Other domestic grey wastewaters	
Kitchen ww.	451 [380; 536]$_{95\%}$
Laundry ww.	101 [89.8; 113]$_{95\%}$
WWTP influent	
Lundtofte ww.	992 [721; 1360*]$_{95\%}$

*extrapolated value

Clear concentration-response relationships were found in all samples, though complete inhibition was not seen in all samples tested in the algal test. In some samples, pronounced stimulation (10-30 % increase in growth rates) occurred at the lower concentrations, but also significant growth rate inhibitions at higher concentrations (***Paper VII***).

4.4.3. Acute willow tests

The normalised transpiration in undiluted samples of grey wastewater and collected rainwater after 72 h is set out in Figure 4. The normalised transpiration is the actual transpiration compared with transpiration of reference willow trees grown in control nutrient solutions. Both kitchen and laundry effluents were found to be toxic to willows. In the laundry wastewater, the wash cycle seems to be more toxic than the whole laundry effluent (Figure 4). The toxicity also appears to be dependent on type and amount of detergent used.

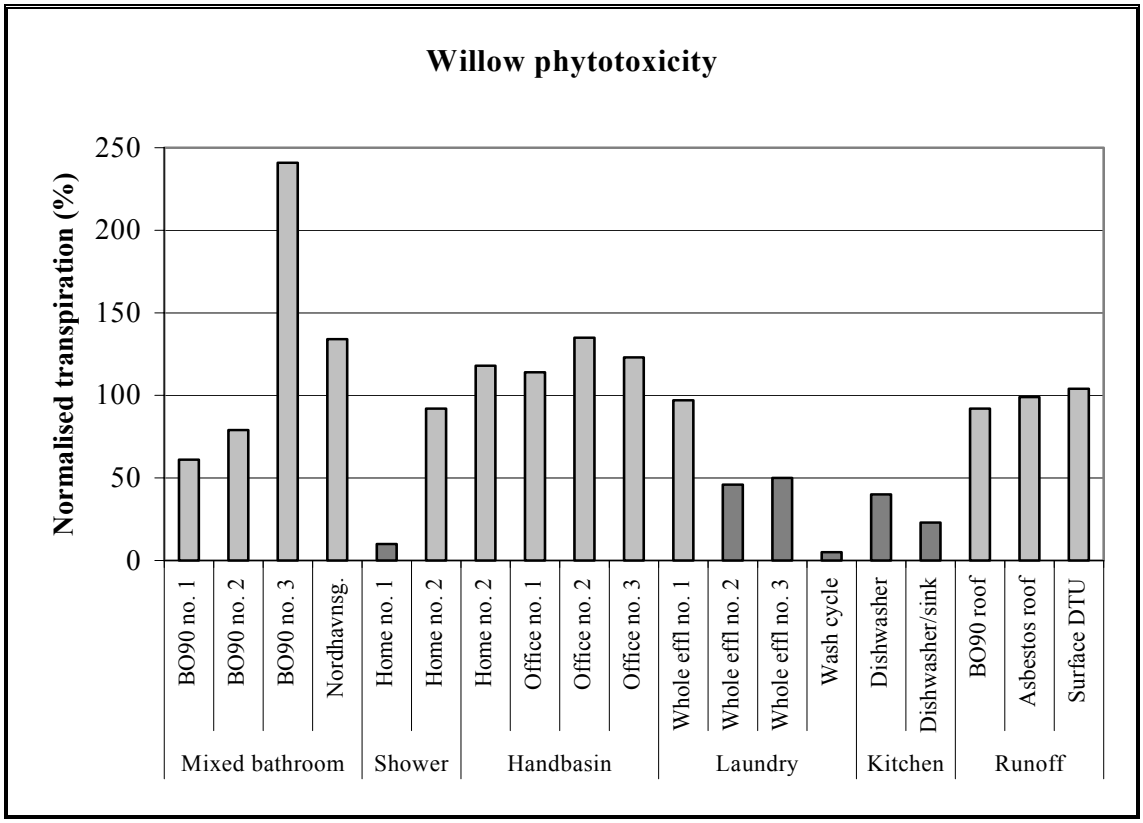

Figure 4. Willow phytotoxicity for different fractions of non-potable water (*Paper VII* and Výmetalova, 2001).

Handbasin wastewater did not show any adverse effect on willows after tests on one domestic and three office building handbasin effluents. In two samples, mixed bathroom wastewater showed a slight negative effect but in two others stimulation was seen. Two shower wastewaters were tested and one was toxic whereas the other was non-toxic (***Paper VII***).

Some but not all of the toxicity detected could be explained by the elevated pH due to the presence of detergents; so the observed toxicity in the laundry sample could perhaps be explained by the contents of detergents. The whole-effluent laundry sample (no. 3 in figure 4) contained three products known to be toxic to fresh water organisms (Daphnia magna) (Pettersson *et al*., 2000; ***Paper VII***). Since no new clothes potentially containing dyes, preservatives, fixatives or flame-retardants were washed during the sample collection period, the detergent and softener products may therefore be major contributors to the toxicity found in the laundry sample in the present study.

No toxicity due to the exposure to roof or surface run-off was seen (Výmetalova, 2001).

Willow evaporation beds are closed systems with the exception of water evaporating, and the concentrations of inorganic ions in the soil will therefore accumulate over time; this was also found in old willow beds, where the electric conductivity was found to increase with age (Stubsgaard, 2001). High concentrations of inorganic ions are toxic for willow trees and the growth of willows will decrease at increased ion concentrations; this is also borne out by old willow beds, which have a lower transpiration and biomass production than young beds (Stubsgaard, 2001). A correlation between phytotoxicity and electrical conductivity was seen, as high electrical conductivity caused an increase in toxicity (***Paper VII*** and Výmetalova, 2001).

5. DO XENOBIOTIC ORGANIC COMPOUNDS POSE A POTENTIAL PROBLEM AND HAZARD?

5.1. SCENARIOS

To evaluate the risk regarding the use of non-potable water, scenarios have to be suggested, exposure routes determined and potential hazards and problems identified.

Three different scenarios for local use of grey wastewater and collected rainwater were selected for evaluation.

- toilet flushing
- in washing machines
- washing of cars and windows

Furthermore, discharge into the environment, i.e. surface waters, irrigation or infiltration into the soil, was also considered (***Paper V*** and ***VI*****;** Eilersen *et al*., 2002; Ledin *et al*., 2002A).

5.2. METHOD FOR RISK ASSESSMENT

5.2.1. Hazard and problem identification

The pathways for human and environmental exposure were identified for each of these applications, followed by identification of potential hazards and problems, see Table 10.

Table 10. Identification of hazards and problems associated with different types of reuse (*Paper VI*, Ledin *et al*., 2002A, Eilersen *et al*., 2002).

Utilisation	Exposure pathway	Potential hazard or problem	Type of hazard/ problem
Toilet flushing	Inhalation of aerosols	Allergies Infectious diseases	Health
	Skin contact	Allergies Infectious diseases	Health
	Others	Colouring of the toilet bowl Foaming Odour Precipitation	Aesthetic Aesthetic Aesthetic Technical
Laundry wash	Skin contact	Infectious diseases Allergies Cancer Mutagenic effects Reproductive effects	Health
	Others	Colouring of cloth Corrosion Odour Precipitation Whitening of cloth	Aesthetic Technical Aesthetic Technical Aesthetic
Wash of cars and windows	Inhalation of aerosols	Allergies Infectious diseases	Health
	Skin contact	Infectious diseases Allergies Cancer Mutagenic effects Reproductive effects	Health
	Others	Corrosion Odour Precipitation	Technical Aesthetic Technical

Local treatment	Biofilter	Toxicity	Technical
Local infiltration	Soil and soil living organisms	Accumulation Deteriorating quality (e.g. changes in soil structure) Toxicity	Environmental
	Groundwater	Deteriorating quality Mobilisation to the groundwater	Environmental
Discharge into surface waters	Surface water and water living organisms	Accumulation Deteriorating quality Toxicity	Environmental
	Swimming	Allergies Cancer Mutagenic effects Reproductive effects	Health

5.2.1.1. Human health hazards

The hazards studied in terms of human exposure routes were inhalation of aerosols and skin exposure. Thus, the identification does not include scenarios where oral exposure can occur e.g. if the water is used for drinking purposes, cooking, for rinsing fruits and vegetables or accidental consumption by small children and household pets from the toilet bowl. The observed and potentially present XOCs were evaluated by collecting information regarding their ability to promote allergic reactions, cancer, mutations, and reproductive effects (CMR). The time for skin contact is different in the toilet flush and the laundry scenario as the toilet flush potentially leads to short contact with drops whereas the pollutants in the laundry water can accumulate in the fabric resulting in a extensive exposure: hence the CMR hazards. The same evaluation needs to be undertaken for swimming, which is a primary source of skin contact with the pollutants in the water.

5.2.1.2. Environmental hazards

The environmental hazards considered where discharge into the environment, either directly into surface water, by irrigation or by infiltration into soil. In respect of the environmental fate of the compounds, the persistence, bioaccumulation, toxicity, and mobility of the inherent properties were noted.

Information on persistence to degradation was gathered for both aerobic and anaerobic conditions. Bioaccumulation, based on the bioaccumulation factor (BCF), was summarised along with acute aquatic toxicity for three trophic levels (fish, crustacean, and algae), measured as effect/lethal concentration (EC_{50}/LC_{50}). Chronic toxicity data are preferred for the hazard identification as they include several stages in the life of the organisms and potentially reproduction steps but acute data can be used to screen for toxicity (Commission of the European Communities, 2001). The potential risk for leaching was assessed by the partition coefficient between organic carbon and water (K_{oc}).

In the hazard identifications, "worst-case" scenarios were used; i.e. the highest BCF and lowest EC_{50} etc. were used according to the precautionary principle (Commission of the European Communities, 2001). The "cut-offs" used in the hazard identifications presented in ***Paper V*** and ***VI*** are listed in Table 11.

Table 11. Chosen cut-off values of the properties P, B, T and mobility

	P	**B (BCF)**	**T (EC/LC_{50}) mg/L**	**Mobility (K_{oc})**
Grey wastewater	Not degradable	>100	<1	-
Collected rainwater	Not degradable	>2000*	<0.1*	<150, 150-2000 >2000, NI

* According to the European Commission (2002)

If no data for bioaccumulation were available, the BCF was estimated from the octanol-water partition coefficient (K_{ow}) using the relationship: $BCF = f_{lipid} \times K_{ow}$ (European Commission, 2002). The lipid content has been set at 10 % as a "worst-case" assumption. The environmental data were retrieved by searching in environmental and chemical databases and handbooks (see ***Paper V*** and ***VI*** and references therein). For the persistence criteria, the European Commission (2002) recommends that compounds with half-life of above 40 days in fresh water or 60 days in marine water should be considered to be problematic; however, it was not possible to implement this in either of the studies as all degradation tests of the present pollutants were found to have been tested in a 5 to 28-day window. Only the criteria "degradable" and "not degradable" were therefore used. K_{oc} was estimated from K_{ow} using the relationship: $K_{oc} = 0.411 \times 10^{logKow}$ (Karickhoff, 1981).

5.2.1.3. Technical and aesthetic problems

Precipitation of metal salts/minerals may constitute a problem e.g. during laundry washes, where the temperature and the pH (due to the presence of detergents) are elevated and several salts/minerals may be close to supersaturation. Other technical and aesthetic problems are, for example, discolouration of the toilet bowl, corrosion, odour due to anaerobic conditions or microbiological growth, and foaming; but also toxicity to biological filters designed to treat the water before reuse. The biofilm in a local biofilter may be affected by compounds present in the raw water fractions, causing disturbances leading to disruption of the treatment process i.e. compromising the treatment of the water (Eilersen *et al*., 2002; Ledin *et al.*, 2002B)

The potential for precipitation, which may cause clogging, was evaluated, using chemical equilibrium calculations in a software for geochemical modelling (PHREEQC; Parkhurst and Appelo, 2001). Calculations were performed as "worst-case" scenarios where the highest concentration of the metals found - Al, Ba, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Pb, Sr and Zn (***Paper I, II, III*** and Ledin *et al*., 2002B) - were used to the modelling process in a total of 18 cases for each of the two water fractions (12 cases presented in ***Paper VI***) with varying pH, alkalinity, temperature, as well as chloride and sulphate concentrations. It was calculated on a neutral pH, a case in which the pH was 10 to simulate the reuse scenario for laundry in which the temperature also elevated to 40 and 60°C. In all simulations alkalinity, chloride and sulphate concentrations was varied within an interval representing minimum and maximum concentration.

5.2.2. Exposure assessment

The PECs can be calculated from actual analysis data or from model outputs. In the exposure assessment of grey wastewater, PECs for the aqueous and solid phases were calculated from concentrations found in the quantitative and semi-quantitative analyses, with the assumption that no removal occurred from the grey wastewater before discharge. A dilution of 100 times with surface water was assumed from the range of dilution factors suggested by the European Commission (2002) of 10 (from wastewater treatment plant effluent to river) to 1000 (from some types of surface waters). PECs in soil were calculated according to exposure models given by the European Commission (2002).

5.2.3. Effects assessment

The effects assessment is an evaluation of the dose-response (concentration-effect) correlation for a selected environmental compartment. For the effects assessment of grey wastewater, PNECs were found in literature or calculated from the lowest of the acute aquatic toxicity data for three trophic levels (fish, crustaceans and algae) as well as an assessment factor of 1000. Assessment factors are used since they reflect the error and uncertainties in extrapolating the test data into the actual environment; hence, for the more detailed

ecotoxicity data available, the lower assessment factor can be used. PNECs in soil were calculated from PNECs in the aqueous phase according to equations given by the European Commission (2002) with the assumption of a standard environment and assuming that compounds which are toxic to water living organisms also are toxic to soil living organisms (European Commission, 2002).

5.2.4. Risk characterisation

The risk characterisation estimated the probability of the incidence of the risk. The risk characterisation for grey wastewater (***Paper V***) was performed on the compounds identified in the environmental hazard identification as potentially problematic. The ratio between PEC and PNEC was calculated and if the result was above 1 the compounds were considered as priority pollutants. However if other dilution or assessment factors had been used in the exposure and the effects assessment, for example assessment factors of 100 or 10 000 instead of 1000, the result would be shifted one tenth potential, making the compounds, which were found in this study to have a ratio of 0.1 to 10, to be of interest.

5.3. RESULTS OF RISK ASSESSMENT

5.3.1. Hazard identification

Hazard identification has been performed on the 201 XOCs found in quantitative and qualitative analyses of grey wastewater as well as for 28 metals and inorganic trace elements. All the 599 constituents quantified in and potentially present in collected rainwater were assessed. All of these constituents were evaluated according to their ability to induce either environmental or human health effects or technical and aesthetic problems.

5.3.1.1. Human health hazards

It was generally difficult to find information on health hazards (allergenic, carcinogenic, mutagenic, and reproductive effects) in relation to the identified compounds. Thus, this kind of information was only found for 45 out of the 229 metals and XOCs in grey wastewater (20%) and for 159, which corresponds to 28% of the 599 constituents in collected rainwater (Table 12 and 14). It was found that 11 compounds in the grey wastewater may provoke allergic reactions, 29 may cause cancer, 15 are mutagenic, and 20 are teratogenic (Table 12).

In Tables 13 and 14 are the metals and XOCs categorised according to the cut-offs given in Table 11. For the persistence criterion are the compounds divided into not degradable (N), degradable (Y) and no information found (NI). The mobility are categorised into mobile constituents (M), constituents that show some mobility (m) and immobile (im).

Table 12. Inherent properties of the constituents observed in chemical analyses of grey wastewater, categorised according to selected cut-off values (Table 11) (from *Paper V* and data found for this thesis)

Hazard classification	No.	P			B (BCF)			T (mg/L)			C	M	R	A	Mobility			
		N	*Y*	*NI*	*>2000*	*>100*	*NI*	*<0.1*	*<1*	*NI*					*M*	*m*	*im*	*NI*
Metals and trace elements	28	28			3	7	15	9	12	13	5		4	5	23			5
Emulsifiers	8	1	7		8	8		2	2	2	1			1			8	
Fragrances & flavours	42	2	16	24	11	24	6		2	23	6	5	4	9	11	17	14	
Miscellaneous	67		6	61	9	10	49	1	2	59	1		1		10	4	42	11
Preservatives & antioxidants	18	2	10	6	3	9	1	4	5	5	5	4	2	1	8	5	4	1
P-triesters	2	2			1	1			1		1	1			1		1	
Softeners & plasticizers	11	1	8	2	2	7		1	7	2	2	2	4		8	2	1	
Solvents	32	1	15	16	8	12	12	1	4	18	7	3	5		9	4	19	
Surfactants	20		10	10	10	11	8	1	3	13	1					2	16	2
UV filters	1			1	1	1				1								1
	229	**37**	**72**	**120**	**56**	**90**	**91**	**19**	**38**	**136**	**29**	**15**	**20**	**16**	**70**	**34**	**105**	**20**

It was found that 73 out of the 599 compounds potentially present in collected rainwater could give rise to allergic reactions, 78 compounds may cause cancer, 13 compounds are known to be mutagenic and 32 can affect reproduction (***Paper VI***). Some of the compounds are known to have more than one of these properties. Pesticides, halogenated and aromatic compounds in particular were found to contain several compounds that were health-hazardous.

Research of relevant literature revealed reports with ecotoxicity tests and tests on cell levels for genotoxicity and mutagenicity but no direct human toxic studies for collected rainwater (Ledin *et al*., 2002A and references therein) and no such information was found for grey wastewater.

Changing cut-off values drastically changes the number of compounds classified as hazardous, as can be seen in column B and T in Table 12. By increasing the toxicity cut-off value from <0.1 to <1 mg/L, the number of compounds classified as hazardous increases to the double.

Extended research of the literature would probably see an increase in the number of compounds for which information becomes available, but it is almost certain that information is not available for all compounds.

Table 13. Inherent properties of the constituents observed and potentially present in collected rainwater, categorised according to selected cut-off values (Table 11) (*Paper VI*)

Hazard classification	No.	P			B (BCF)			T (mg/L)			C	M	R	A	Mobility			
		N	*Y*	*NI*	*>2000*	*>100*	*NI*	*<0.1*	*<1*	*NI*					*M*	*m*	*im*	*NI*
Metals and trace elements	30	29		1	3	7	16	10	15	12	6		4	5	30			
Aliphatic amines	6		4	2		1	2			3				2	3	2		1
Alkanes	24	3	2	19	3	4	18	2	2	19	14			1	1	1	20	2
Aromatic hc.	27	3	12	12	3	9	9	1	7	9	6	2	5	8	7	9	10	1
Chlorophenyls	1			1			1			1								1
Dioxins & furans	28	1		27	6	7	21	3	3	25							15	13
Ethers	13	1		12		1	11			11	1			1	7		3	3
Halo. aliph. hc	37	12	13	12	1	3	9	4	5	10	11	2	5		30	4	2	1
Halo. arom. hc	32	2	12	18	3	16	11	4	12	12	4			5	8	11	11	2
Miscellaneous	149	12	29	108	9	15	105	1	5	107	7	1	5	19	49	13	30	57
Organolead comp.	12			12	2	2	10	1	2	10			10			1	1	10
Organotin comp.	9		1	8	1	1	8	2	2	7				3	1	2	3	3
PCBs	22			22	6	6	16	5	6	16						31	21	1
Pesticides	102	15	21	66	15	28	47	38	43	49	20	6	2	22	29	8	29	13
Phenols	47	6	18	23	5	12	22	4	11	21	2			6	22		8	9
Softeners & plasticizers	9		8	1	2	4	1	2	5	1					2		6	1
PAHs	48	4	8	36	13	18		6	12	35	7	2	1	1	1	2	31	14
P-triesters	3		3	0	1	2	29	1	2								3	
	599	**88**	**131**	**380**	**73**	**136**	**336**	**84**	**132**	**348**	**78**	**13**	**32**	**73**	**190**	**84**	**193**	**132**

5.3.1.2. Environmental hazards

Environmental hazard identification was hampered by the lack of information on environmental data, especially for persistence to degradation; as for a majority of the compounds, only data for aerobic conditions were found and no information of potential anaerobic degradation.

Data on minimum of one parameter (degradation, bioaccumulation and toxicity) were found for 143 compounds out of the 229 metals and XOCs found in grey wastewater, whereas for the remainder no data were found. A total of 9 organic compounds were found to be persistent to degradation whereas 72 were found to be degradable (Data from ***Paper III*** and ***V***) see Table 12. Ninety compounds were found to be potentially bioaccumulating (BCF>100) whereas for 91, no data on bioaccumulation were found. 38 compounds were found to be highly toxic to aquatic organisms (EC_{50}/LC_{50} <1mg/L) (see Table 12). Several compounds commonly used in personal care products such as skin creams e.g. isopropyl myristate and citric acid were found to be readily biodegradable, non-toxic and not bioaccumulating (***Paper V***).

Data on a minimum of one parameter (degradation, bioaccumulation and toxicity) were found for 290 compounds out of the 599 organic constituents potentially present in collected rainwater, whereas for the remainder no data were found. One hundred and thirty one compounds were found to be degradable (aerobic and/or anaerobic) and 88 were persistent to degradation. Data on bioaccumulation were found for 263 compounds, and 73 were classified as bioaccumulating (BCF>2000, Table 13). A total of 167 compounds were non-toxic, according to the European Commission (2002) toxicity criterion of EC/LC_{50} <0.1 mg/L and 84 were found to be toxic (***Paper VI***). The criterion often used in the aquatic system of <1

mg/L as "very toxic to water living organisms" revealed 132 very toxic compounds i.e. changing the cut-off values changes the number of compounds in each group.

Of the 229 compounds present in grey wastewater, 209 were classified according to the partition coefficient between organic carbon and water K_{oc}. 70 were found to be mobile (M), 34 slightly mobile (m) and 105 immobile (im) (Data from ***Paper III*** and this thesis) (Table 12).

In collected rainwater, 467 compounds were classified and of these, 190 were categorised as mobile (M), 84 as slightly mobile (m) and 193 as immobile (im) (Table 13) (***Paper VI***).

The halogenated aliphatic hydrocarbons, the miscellaneous, the pesticides and the phenols all contain a large number of highly mobile compounds i.e. they present a potential risk of leaching into the groundwater whereas the alkanes, aromatic hydrocarbons, miscellaneous, PCBs, pesticides and PAH contain several compounds that are immobile.

The halogenated aliphatic hydrocarbon, miscellaneous and pesticide group had the highest number of compounds that were found to be persistent to degradation. The pesticides and the PAHs groups contained the highest number of bioaccumulating compounds and the pesticide group also contributed the highest number of toxic compounds: 38 out of 102 pesticides were found to have a EC_{50}/LC_{50} <0.1 mg/L. However, more information is generally available on pesticides than on the other compound groups. This is of course unfavourable to the pesticide group as it is likely that more compounds in the other groups would be categorised as hazardous if more information were available.

This type of classification is hampered by the limited information available on biodegradation, toxicity and bioaccumulation in respect of a large number of the compounds. For a majority of the compounds, only information on aerobic degradation was reported, making the identification weak as only aerobic conditions could be assessed. The possibility can therefore not be ruled out that the number of compounds listed as potentially problematic pollutants would increase dramatically if more information were available. The results show that the compounds found in grey wastewater and collected rainwater constitute a potential hazard to the environment if the water is used, without previous treatment, for irrigation, infiltration or to preserve wetlands.

5.3.1.3. Technical and aesthetic problems

Discolouring of clothes or the toilet bowl could be caused by precipitation of metal-(hydr)-oxides, or the presence of natural organic matter such as humic and fulvic acids. Foaming can occur due to organic compounds with a lipophilic and hydrophilic moiety e.g. detergents, fatty acids, proteins etc. Furthermore, may microorganisms cause odour and discolouring due to growth.

Geochemical modelling showed that precipitation of minerals is possible in grey wastewater containing Al, Ba, Fe, K and possibly Ca, Pb and Zn whereas the laundry scenario with elevated temperatures and pH also showed potential for precipitation of Ca, Mg, Mn, Pb, Sr and Zn-(hydr)-oxides, and possibly Cd (simulations based on data from ***Paper I***, ***Paper III***, Ledin *et al*., 2002B) (Table 14).

Table 14. Results from geochemical modelling of elements in grey wastewater. Notification + means that the water is supersaturated with the current metal, - means that the water is undersaturated with the minerals containing the metal and ± means that the system is in equilibrium, i.e. + and ± indicate a potential for precipitation.

			pH 7 Temp. 20°C (Data from ***Paper I***; ***III;*** Ledin *et al*., 2002B)						**pH 10 Temp. 40°C** (Data from ***Paper I***; ***III;*** Ledin *et al*., 2002B)						**pH 10 Temp. 60°C** (Data from ***Paper I***; ***III;*** Ledin *et al*., 2002B)					
	Alkalinity (meq/l) as HCO_3^-		**1.0**		**12**		**340**		**1.0**		**12**		**340**		**1.0**		**12**		**340**	
	Chloride (mg/l)		**9.0**	**90**	**9.0**	**90**	**9.0**	**90**	**9.0**	**90**	**9.0**	**90**	**9.0**	**90**	**9.0**	**90**	**9.0**	**90**	**9.0**	**90**
	Sulphate (mg/l)		**12**	**160**	**12**	**160**	**12**	**160**	**12**	**160**	**12**	**160**	**12**	**160**	**12**	**160**	**12**	**160**	**12**	**160**
Metal	Al	3.55	+	+	+	+	+	+	-	±	±	±	±	±	-	-	-	-	-	-
	Ba	0.12	±	+	±	+	±	+	-	+	-	+	-	+	-	±	-	±	-	±
	Ca	102	-	-	-	-	±	±	+	±	+	+	+	+	±	±	+	+	+	+
	Cd	0.001	-	-	-	-	-	-	-	-	-	-	±	±	-	-	-	-	±	-
	Cu	0.39	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Fe	4.37	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
	K	7.4	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-
	Mg	23.0	-	-	-	-	-	-	±	±	+	+	+	+	±	±	+	+	+	+
	Mn	0.08	-	-	-	-	-	-	+	+	+	+	+	+	+	+	+	+	+	+
	Na	480	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Pb	0.15	-	-	-	-	±	±	+	+	+	+	+	+	+	+	+	+	+	+
	Sr	2.29	-	-	-	-	-	-	-	-	-	±	+	+	±	±	±	±	+	+
	Zn	6.30	-	-	-	-	±	±	+	+	+	+	+	+	+	+	+	+	+	+

The collected rainwater may be expected to precipitate minerals containing Al, Cd, Fe, K, Pb and possibly Ba, Ca, Mg, Mn and Zn that potentially will cause clogging. With washing machines, which use rainwater, there is also a risk of precipitation of Al, Ca, Cd, Fe, Mg, Mn, Pb and Zn but not Ba and K (***Paper IV*** and data from ***Paper II***) (Table 15). The concentration of metals found in rainwater is generally several times higher that that found in grey wastewater due to the lack of point sources e.g. metal roofing. The scenarios are worst-cases scenarios i.e. the highest levels found for the respective constituent has been used.

Table 15 Results from geochemical modelling of elements in collected rainwater. Notification + means that the water is supersaturated with the current metal, - means that the water is undersaturated with the minerals containing the metal and ± means that the system is in equilibrium, i.e. + and ± indicate a potential for precipitation.

			pH 7 Temp 20°C (*Paper VI*)						pH 10 Temp 40°C (*Paper VI*)						pH 10 Temp 60°C (Data from *Paper II)*					
	Alkalinity (meq/l)		**1.4**			**326**			**1.4**			**326**			**1.4**			**326**		
	Chloride (mg/l)		**50**		**46000**	**50**		**46000**	**50**		**46000**	**50**		**46000**	**50**		**46000**	**50**		**46000**
	Sulphate (mg/l)		**10**	**680**	**10**	**10**	**680**	**10**	**10**	**680**	**10**	**10**	**680**	**10**	**10**	**680**	**10**	**10**	**680**	**10**
Metal	Al	71.3	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
	Ba	0.12	-	±	-	-	±	-	-	-	-	-	-	-	-	-	-	-	-	-
	Ca	480	-	-	-	±	±	±	-	-	±	+	+	+	-	-	-	+	+	+
	Cd	0.70	-	-	-	+	+	-	+	+	-	+	+	±	±	±	-	+	+	±
	Cu	6.80	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Fe	78.6	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
	K	13.7	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-
	Mg	39.7	-	-	-	-	-	±	-	-	-	+	+	+	-	-	-	+	+	+
	Mn	1.65	-	-	-	±	±	±	+	+	+	+	+	+	+	+	+	+	+	+
	Na	67000	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Pb	2.76	±	±	-	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
	Sr	0.23	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Zn	38.1	-	-	-	±	±	±	+	+	+	+	+	+	+	+	+	+	+	+

Depending on the given concentrations and combinations of compounds, exposure to XOCs may result in inhibition of the biological processes in the biofilter and thereby reduce the effect of the treatment. To investigate this situation, tests of the biological activity in the biofilter were conducted in the form of oxygen uptake rate (OUR) respiration test (Dircks *et al*., 1999) whereby inhibition of respiration due to the exposure of pollutants in the water fraction was measured. No inhibition due to grey wastewater from BO90 was found (Ledin *et al*., 2002B).

The inhibition of the nitrification process was also tested according to a method established by Environment & Research (2002B). But no inhibition but rather a slight stimulation effect was detected. The weak stimulating effect may be caused by the presence of micronutrients in the grey wastewater (Ledin *et al*., 2002B).

5.3.2. Exposure assessment

An exposure assessment was conducted on the compounds identified as hazardous in the hazard and problem identification. Concentrations from the semi-quantitative and quantitative analyses were used to calculate PECs for two scenarios: receiving water (lake) and soil (closed treatment bed). For the lake scenario, they ranged from 0.004 µg/L (PCP) to 0.45 µg/L (LAS). For the soil scenario PEC_{soil} was found to be in the range of 1×10^{-5} mg/kg soil for PCP to 0.11 mg/kg for LAS (***Paper V***).

5.3.3. Effects assessment

PNECs were calculated in the effects assessment for the compounds identified as hazardous in grey wastewater**.** For the lake scenario, it was only possible to calculate PNECs for 32 out of the 39 potentially problematic pollutants due to the lack of information on acute aquatic toxicity to, fish, crustaceans and algae. $PNEC_{soil}$ was calculated from $PNEC_{water}$ i.e. assuming that what is toxic to aquatic organisms is also toxicity to soil-dwelling organisms (European Commission, 2002). In a few cases it was not possible to find the partition coefficient between soil and water K_D or the inherent properties needed to calculate it - e.g. K_{oc} (or K_{ow}), or vapour pressure and water solubility - so it was only possible to calculate $PNEC_{soil}$ for 28 out of the 39 potentially problematic pollutants (***Paper V***).

No effects assessment was made for collected rainwater.

5.3.4. Risk characterisation

In the risk characterisation, PECs from the exposure assessment and PNECs from the effects assessment were compared and it was found that for the aquatic scenario the ratio >1 applied to only 5 of the compounds. Further refinement of the data including abiotic degradation rates indicated that 4 of the compounds have a ratio PEC/PNEC >1 (***Paper V***). For the soil bed, only four compounds resulted in ratios of above 1, although ratios for compounds with $\log K_{ow}$ >5 were increased 10 times as recommended by European Commission (2002) (Table 16).

Table 16. Risk characterisation of XOCs in grey wastewater

Lake scenario	PEC (µg/L)	PNEC (µg/L)	Ratio	Soil scenario	PEC (µg/kg)	PNEC (µg/kg)	Ratio
Dibutyl phthalate	0.03	0.003	9.1	Dibutyl phthalate	0.76	0.16	4.7
LAS	4.50	0.90	5.0	Hexyl cinnamic aldehyde	0.17	0.07	2.5
Malathion	0.02	0.001	36.6	LAS	110	14	7.9
Triclosan	0.01	0.002	4.0	Malathion	0.47	0.02	30.6

Four compounds were found to have a PEC/PNEC ratio between 0.1 and 1, using an assessment factor of 1000, 1-dodecanol, DEHP, N,N-dimethyl-1-dodecanamine and nonylphenol. If instead an assessment factor of 10,000 had been used the ratio of these compounds hade been above one, whereas if an assessment factor of 100 had been used only malathion would have had a ratio above one. This indicates that careful consideration must be taken to which assessment factors are used as the number of compounds identified as priority pollutants depend on it.

Ibuprofen, paracetamol and acetylsalicylic acid were found to have a PEC/PNEC above 1 in a risk assessment of the 25 most commonly used pharmaceutics in Denmark (Stuer-Lauridsen *et al*., 2000).

6. CONCLUSIONS

An methodology for identifying constituents especially XOCs that may cause hazards and problems in connection with non-potable reuse in households has been developed and successfully tested with two water fractions: grey wastewater and collected rainwater.

The methodology was found to be promising, and could be extended towards a realistic risk assessment.

6.1. GREY WASTEWATER

It can be concluded that the previous knowledge about the characteristics of grey wastewater (physical, chemical and biological constituents) is limited. The information available in the relevant literature shows that the focus has hitherto been on the content of oxygen-consuming compounds, nutrients and microorganisms. A few studies have included measurements of heavy metals, while information about the presence and levels of specific XOCs is very limited. It was also found that grey wastewater from different sources has different characteristics and this illustrates the need for different types of treatment before any recycling of water.

No evaluation of environmental and health risks connected with physical and chemical constituents could be found in the literature.

A list over XOCs potentially present in grey wastewater was drawn up based on product information, consumption statistics and the available knowledge on the presence of XOCs in domestic wastewater. The number of different compounds and compounds groups in that list reached 900.

In an investigation of consumption of household chemicals in a multi-family dwelling, 92 different household chemicals and personal care products were recorded. The inhabitants' average weekly consumption was about 40 g per person. The inventory of declarations of contents of household chemicals and personal care products registered a total of 290 chemical constituents.

By comparison it was found that the list of 900 potentially present compounds and 290 constituents recorded on household chemical products intersected with 94 different XOCs. The prime distinction was found for the fragrances as hardly any matches between the two lists were seen.

201 different XOCs were identified in grey wastewater from bathrooms (showers and handbasins). Several fragrances such as like citronellol, coumarin and hexyl cinnamic aldehyde were identified as well as some preservatives e.g. parabens and triclosan. The measurements also showed that bioactive chemicals (pharmaceuticals) were present, as well as unexpected chemicals not directly deriving from household chemicals e.g. flame-retardants and drugs. The presence of detergents, softeners, and preservatives among others was confirmed.

Quantitative analyses of fatty acids (C_6 to C_{20}) showed that the dominating organic acids in grey wastewater from bathrooms are lauric acid (C_{12}), palmitic (C_{16}) and stearic acid ($C_{18:0}$). In the drinking and hot tap water used to produce the grey wastewater, low levels of the fatty acids were found, which indicates that the acids present in grey wastewater originate from the hygiene products used, e.g. soap and skin creams. High levels, up to 27 mg/L, were found.

It has been shown that it is possible to track the potentially toxic compounds used in households that may present a problem, e.g. in relation to infiltration of grey wastewater. However, the observations made in this study illustrate that an inventory of household chemicals used, although detailed and careful, cannot represent full characterisation of the compounds actually present in grey wastewater.

Some types of grey wastewater (kitchen and laundry) were found to be toxic to willow trees and freshwater green algae whereas other types did not result in measurable toxic effects. The toxicity of laundry wastewater may be related to the toxicity of the detergents used.

In total, 39 out of the 201 XOCs found to be present in the grey wastewater from bathrooms were listed as potentially problematic pollutants in environmental hazard identification based on persistence, bioaccumulation and toxicity.

An environmental risk characterisation of the 201 organic compounds revealed that five compounds constitute as risk if direct discharged into surface water or into a soil bed

6.2. COLLECTED RAINWATER

The number of organic, inorganic, and microbiological constituents found to be present in collected rainwater is high. The data shows that there is a large variation between different sites due to different climate, urban environment and land use. It has been established that the majority of the studies have focussed of run-off from roads and roofs, as well as unspecific stormwater.

The number of constituents that have been identified and quantified in collected rainwater is probably only a fraction of those compounds that might be present, as even a limited search of potential sources and their contribution resulted in a list of several hundreds of constituents.

There was no evidence of any adverse effects towards willows trees caused by collected rainwater tested in an acute willow assay.

The number of compounds that constitute a potential environmental hazard with respect to the direct discharge into receiving waters or irrigation and infiltration into soil of collected rainwater is high.

6.3. GENERAL CONCLUSIONS

The human health hazard identification revealed a large number of potential hazardous constituents in both water fractions, which may present a health problem if exposed to the skin, or inhaled.

In the technical and aesthetic problem identification it was found that some metal salts/mineral may precipitate and potentially cause clogging and discolouration. Several minerals are close to supersaturation in conditions with high temperature and pH that occur during laundry wash, which makes this application more exposed to precipitation.

The health and environmental hazard identifications were hampered by the lack of data on the identified constituents.

The content of metals and XOCs are to be considered if either water fraction is to be used for domestic reuse or discharge since if untreated it is potentially toxic to humans and plants and may pollute the groundwater.

7. SUGGESTIONS FOR FURTHER RESEARCH

The methodology and the methods used in this thesis can be applied to other types of water fractions for reuse e.g. municipal and industrial wastewater and also in other climatic or cultural regions. The scenarios could also be extended to include other domestic non-potable reuses e.g. cooling systems. Furthermore, the case study of rainwater could also be expanded to include rainwater characterisation, surface and source investigations followed by characterisation of the collected rainwater.

The issue of treatment should be studied as the number of small treatment plants will increase and thereby a strong demand for information on appropriate procedures and technologies. Planning design, construction, operation, maintenance, and control of small plants will differ from large plants due to for example load, flow etc. so treatment requirements and alternatives have to be studied carefully. Furthermore should e.g. energy consumption, economical and social aspects be investigated along with health issues and environmental impacts. A general review of best management practice should be undertaken, incorporating not only state-of-the-art techniques but also with a view to designing an assessment method for their application.

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9. LIST OF ABBREVIATION

A	Classification as promoter of allergic reactions
Aromatic hc.	Aromatic hydrocarbons
B	Bioaccumulating
BCF	Bioaccumulation factor
BHA	Butylated hydroxyanisole
BHT	Butylated hydroxytoluene
BOD	Biological oxygen demand
CMR	Classification as carcinogenic, mutagenic or reproduction toxicant.
COD	Chemical oxygen demand
C_X	Fatty acids, the number indicate the number of carbons in the chain
DEHP	Di (2-ethylhxyl) phthalate
Halo. aliph. hc.	Halogenated aliphatic hydrocarbons
Halo. arom. hc	Halogenated aliphatic hydrocarbons
K_D	Partition coefficient between soil and water
K_{OC}	Partition coefficient between organic carbon and water
K_{OW}	Partition coefficient between octanol and water
LAS	Linear alkyl benzene sulfonates
OUR	Oxygen uptake rate
P	Persistence
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PCP	Pentachlorophenol
PEC	Predicted environmental concentration
PNEC	Predicted no-effect concentration
T	Toxicity
XOCs	Xenobiotic organic compounds

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